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John A. Brown

THE SYNTHESIS OF BICYCLO(2,2,1)-2,5-HEPTADIENE AND BICYCLO(2,2,2)-2,5-OCTADIENE AND RELATED COMPOUNDS

A THESIS

Presented to

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Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School

of Chemistry

By

John Angus Brown

July, 1954

THE SYNTHESIS OF BICYCLO(2,2,1)-2,5-HEPTADIENE AND BICYCLO(2,2,2)-2,5-OCTADIENE AND RELATED COMPOUNDS

Approved:

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Date approved by chairman: October 29, 1954

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I would like to express my appreciation to my thesis director, Dr. Jack Hine, for the guidance, assistance, and gentle prodding which carried me to success; to the Office of Ordnance Research, U. S. Army, whose grant made the work financially possible; and to Mr. Leon Zalkow for his co-operation in our mutual project.

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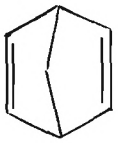
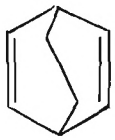
ABSTRACT

The purpose of this investigation was to prepare the compounds bicyclo(2,2,1)-2,5-heptadiene (I) and bicyclo-(2,2,2)-2,5-octadiene (II) in order to secure compounds having a bond structure consisting of



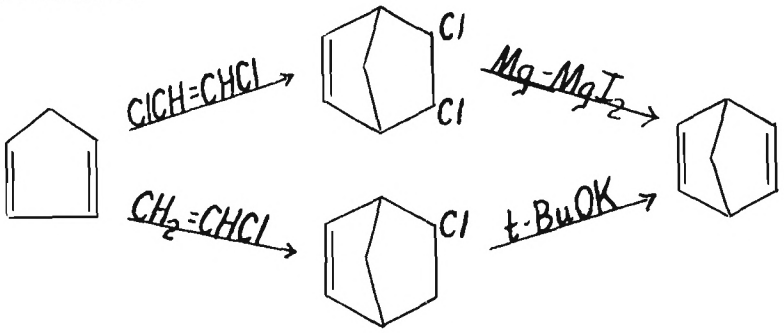
I



II

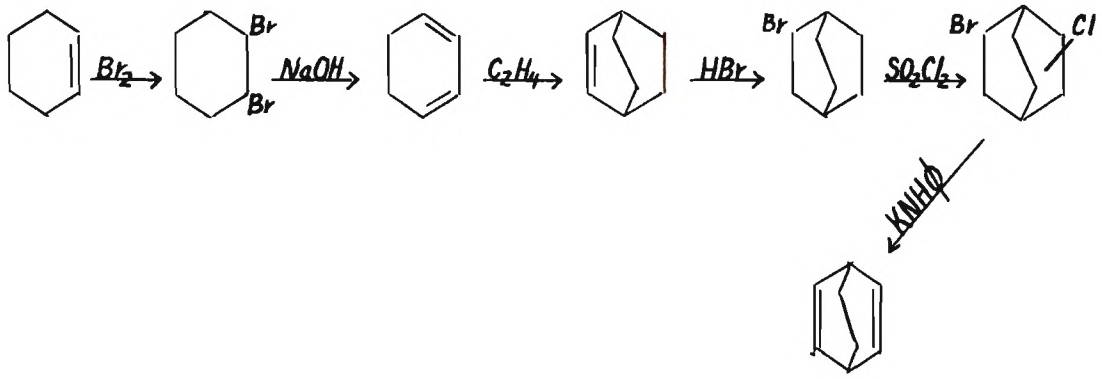
carbon-carbon double bonds which are separated by two carbon-carbon single bonds (so that no conventional resonance structures are possible), but which are close enough to one another spatially so that overlapping of the pi orbitals of the unsaturated carbon atoms might occur. It was felt that such overlapping might result in resonance-type interaction of non-conjugated double bonds, and furnish a convenient test of the theory of pi orbital unsaturation.

Compound I was prepared by means of the following reaction schemes:



In the first instance, commercial dicyclopentadiene was condensed in a high-pressure apparatus with trans-dichloroethylene to give 2,3-dichlorobicyclo(2,2,1)-5-heptene. This was then dehalogenated, using a reactive mixture of magnesium metal and magnesium iodide which is effective under mild conditions, to the desired compound, bicyclo(2,2,1)-2,5-heptadiene. In the second instance, commercial dicyclopentadiene was condensed in a high-pressure apparatus with monomeric vinyl chloride to give 2-chlorobicyclo(2,2,1)-5-heptene. This was then dehydrohalogenated to the desired compound, using a suspension of solid potassium t-butoxide in t-butyl alcohol and distilling the mixture to dryness.

Compound II was prepared by means of the following reaction scheme:



Commercial cyclohexadiene was brominated and then doubly dehydrohalogenated, by means of sodium hydroxide in ethylene glycol, to 1,3-cyclohexadiene. This was condensed in a high pressure apparatus with ethylene gas to give bicyclo(2,2,2)-2-octene. Hydrogen bromide was added to the octene at low

temperature to give 2-bromobicyclo(2,2,2)octane which, upon chlorination with sulfuryl chloride, gave a mixture of isomers of chloro-2-bromobicyclo(2,2,2)octane. This material was doubly dehydrohalogenated, using potassium anilide in refluxing aniline, to the desired compound, bicyclo(2,2,2)-2,5-octadiene.

The identities of these two new compounds (I and II) were proven by quantitative hydrogenation to the known saturated hydrocarbons, by their analyses, and, in the case of II, by pyrolysis products and an analyzed derivative.

Infrared absorption spectra for all important compounds are given in an appendix, as are ultraviolet absorption spectra for bicyclo(2,2,1)-2-heptene, bicyclo(2,2,1)-2,5-heptadiene, bicyclo(2,2,2)-2-octene, and bicyclo(2,2,2)-2,5-octadiene.

The study of the properties of the bond systems and their interactions through overlapping of the pi orbitals is part of a continuing project and will be studied further by other investigators.

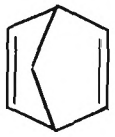
CHAPTER I

INTRODUCTION

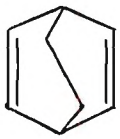
CHAPTER I

INTRODUCTION

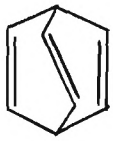
This investigation was undertaken in order to study certain bond structures and their relation to conjugation theory, although the present writer's work has been limited to synthesis. The three compounds bicyclo(2,2,1)-2,5-heptadiene (I), bicyclo(2,2,2)-2,5-octadiene (II), and bicyclo(2,2,2)-2,5,7-octatriene (III) all have double bonds which are not conjugated in the ordinary sense, since they are separated by two single bonds.



I



II

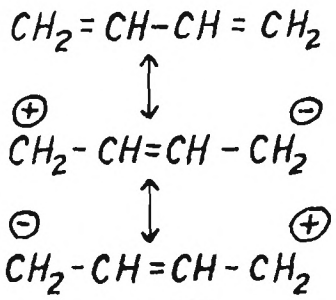


III

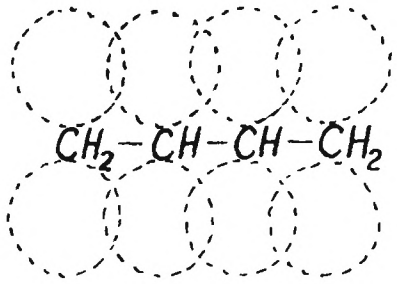
Moreover, these single-bond systems include a carbon bridgehead so that no structure can be written in which there are double bonds alternating with single bonds.

Nevertheless, it was felt that the double bonds in these systems possessed interaction possibilities due to the spatial overlap of their pi orbitals. For example, it is accepted practice to picture the resonance interaction in the butadiene molecule both by the conventional resonance formulas (IV) and by the indication of pi orbital overlap on

the carbon atoms, as is shown in drawing (V).

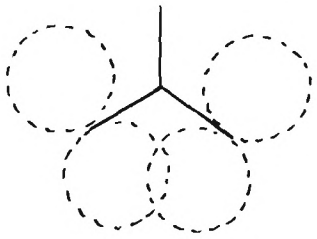


IV

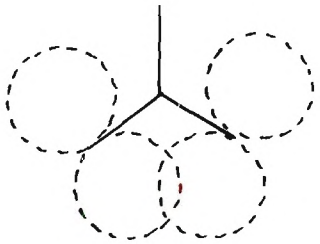


V

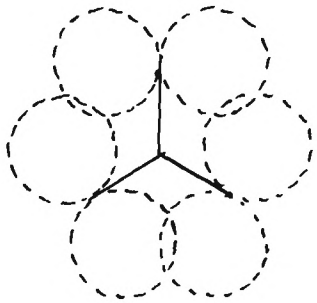
If structures I, II, and III are redrawn using this second concept (I', II', and III'), it may be seen that the pi orbitals from adjacent double bonds lie very close together in space. (In these views, the molecules are shown from the "top," in the sense of drawings I, II, and III.)



I'



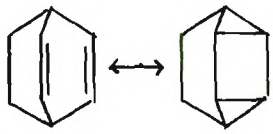
II'

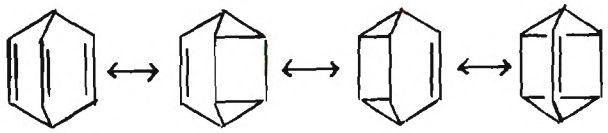


III'

If these pictures of pi orbital interaction are valid, one may expect these isolated double bonds to act as if they were conjugated, leading to such phenomena as 1,5 addition. In the case of III, the overlapping pi orbitals may be expected to form a complete circle, without reactive ends, as in the case of the benzene molecule. Therefore III may actually be expected to show some aromatic character.

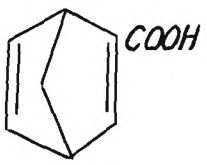
It should be noted at this point that one can draw valence bond resonance structures of a sort for these molecules (VI and VII), but that these structures involve formation of valence bonds between atoms which are somewhat farther apart than the normal carbon-carbon single bond distance.

VI 

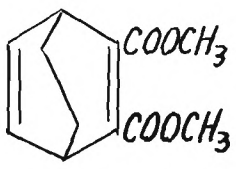
VII 

At the time this investigation was begun, the synthesis of none of these compounds had been reported, although there is a fairly extensive literature covering bicyclic compounds which may be considered as derivatives of these.

Diels and Alder have reported a number of addition reactions involving the dienes cyclopentadiene and cyclohexadiene, including such products as 2-carboxybicyclo(2,2,1)-2,5-heptadiene (VIII) (1) and 2,3-carbomethoxybicyclo(2,2,2)-2,5-octadiene (IX) (2), which contain two of the bond systems



VIII



IX

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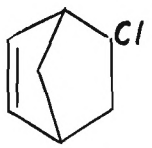
(1) K. Alder, G. Stein, S. Schneider, M. Liebmann, E. Rolland, and G. Schulze, Ann., 525, 183 (1936).

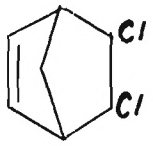
(2) O. Diels, K. Alder, and H. Nienberg, Ann., 490, 236 (1931).

in question, but which also have substitutents which would interfere with an investigation of the properties of these bonds.

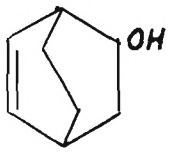
A number of compounds which might serve as immediate precursors of the desired compounds have been reported. Among these are 2-chlorobicyclo-(2,2,1)-5-heptene (X) (3), 2,3-dichlorobicyclo(2,2,1)-5-heptene (XI) (3), and 2-hydroxy-bicyclo(2,2,2)-5-octene (XII) (3).



X

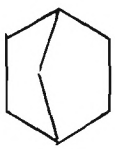


XI

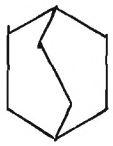


XII

The saturated hydrocarbons, bicyclo (2,2,1)heptane (XIII) and bicyclo(2,2,2)octane (XIV), which could serve both as starting materials and as derivatives of the desired compounds for the purpose of identification have also been reported (4,5,6).



XIII



XIV

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(3) K. Alder and H. F. Rickert, Ann., 543, 1 (1940).

(4) R. Seka and O. Tramposch, Ber., 75B, 1379 (1942).

(5) G. Komppa, Ber., 68B, 1267 (1935).

(6) C. L. Thomas, Ind. Eng. Chem., 36, 310 (1944).

There are a number of model procedures available in the literature for such operations as halogenation (5,7), dehalogenation (8), hydrochlorination (9), dehydrohalogenation (3), dehydration (3), and many others. An excellent summary and bibliography of the bicyclic systems may be found in Elsevier (10).

Since this investigation was begun, Parham, Hunter, Nanson, and Lahr have reported the preparation of a small amount of material which was probably bicyclo(2,2,1)-2,5-heptadiene (11). This compound was prepared by the Chugaev degradation of dehydronorborneol and it reacted with phenyl azide to give a product having the composition of one mole of diene plus two of phenyl azide. These workers point out that the compound is not formed easily, attempted preparation by the acetate pyrolysis method and the Hofmann degradation of the quarternary ammonium hydroxide being unsuccessful.

The use of bicyclo(2,2,1)-2,5-heptadiene as an intermediate in preparing the insecticide Aldrin is reported

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(7) J. D. Roberts, L. Urbanck, and R. Armstrong, J. Am. Chem. Soc., 71, 3049 (1949).

(8) R. K. Summerbell and R. R. Umhoefer, J. Am. Chem. Soc., 61, 3016, 3020 (1939).

(9) L. Schmerling, J. Am. Chem. Soc., 68, 195 (1946).

(10) Elsevier's Encyclopaedia of Organic Chemistry, Edited by E. Joseph and F. Radt. New York-Amsterdam: Elsevier Publishing Co., Inc., 1948, Vol. 12-A, pages 532 ff.

(11) W. E. Parham, W. T. Hunter, R. Hanson, and T. Lahr, J. Am. Chem. Soc., 74, 5646 (1952).

in a patent by Lidov (12). In this patent, the preparation of the diene is not described but is said to be the subject of a pending patent application (13).

Recently, it was learned here that considerable work had been done with this compound by still another investigator whose work was continuing. He reported to us that bicyclo-(2,2,1)-2,5-heptadiene does show certain anomalies, including 1,5 addition (14).

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(12) R. E. Lidov, U. S. Patent 2,635,977 (April 21, 1953) assigned to the Shell Development Company.

(13) Hyman, Freirich, and Lidov, Patent Application U. S. Serial No. 45,574.

(14) S. Winstein, Private Communication.

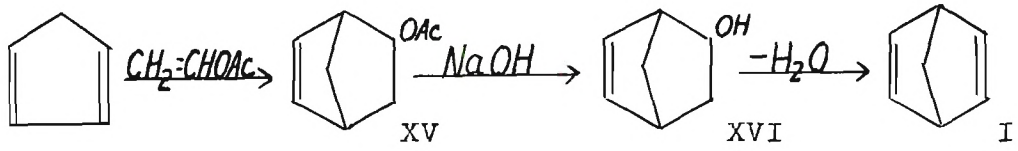
CHAPTER II

RESULTS AND DISCUSSION

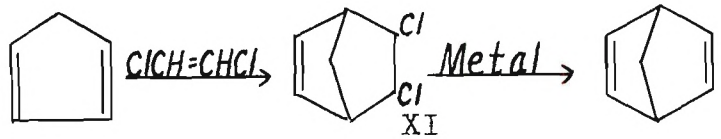
CHAPTER II

RESULTS AND DISCUSSION

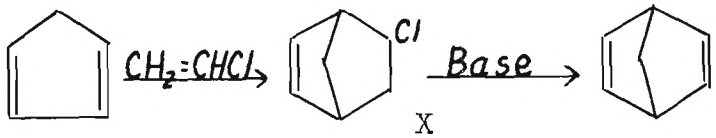
Bicyclo(2,2,1)-2,5-heptadiene.—It was originally planned to attempt the synthesis of bicyclo(2,2,1)-2,5-heptadiene (I) by one or more of the following reaction schemes:



XV XVI I



XI I



X I

Attempts to carry out the first of these three schemes failed; the other two were successful and (I) was prepared by both methods.

In all these reactions, it was deemed desirable to employ reagents which would not be expected to attack the double bonds, and which would be effective under mild conditions in order to avoid the reverse-Diels-Alder decomposition of the adducts which occurs at elevated temperatures. High-temperature pyrolysis and the use of sulfuric acid, for

example, were to be avoided. Also to be avoided were reagents known to lead to rearrangements of the carbon skeleton in similar reactions, such as silver bromide (15) and sulfuric acid (16).

Dehydronorborneol (XVI) was prepared by the alkaline hydrolysis of its acetate (XV), made from cyclopentadiene and vinyl acetate by the method of Alder and Rickert (3). Several attempts to dehydrate this alcohol with phosphorus pentoxide in various solvents, a method which is reported to give norbornylene from norborneol (3), gave no product boiling below 130°. An attempt to dehydrohalogenate 2-chlorobicyclo(2,2,1)-5-heptene (X) by means of boiling quinoline also failed, as did the attempted dehalogenation of 2,3-dichlorobicyclo(2,2,1)-5-heptene (XI) by metallic zinc and by sodium iodide in acetone.

The first successful preparation of the desired bicyclo(2,2,1)-2,5-heptadiene (I) was accomplished by the magnesium-magnesium iodide dehalogenation of 2,3-dichlorobicyclo(2,2,1)-5-heptene (XI), using a modification of the method of Summerbell and Umhoefer (8).

This material was found to be a mobile, water-white liquid boiling at 89.5° at atmospheric pressure, with an

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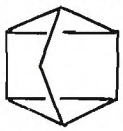
(15) W. von E. Doering and M. Farber, J. Am. Chem. Soc., 71, 1514 (1949).

(16) M. S. Newman and Y. T. Yu, J. Am. Chem. Soc., 74, 507 (1952).

index of refraction of 1.467 and a density of 0.8992 at 26°. These values lead to an observed molecular refractivity of 28.87, compared to a calculated value of 29.19 for structure (I). A carbon-hydrogen analysis by Clark Microanalytical Laboratory gave results in agreement with the assigned formula of C_7H_8. A sample of the compound in ethanolic solution in the presence of Adam's Platinum Catalyst was found to absorb two moles of hydrogen per mole of hydrocarbon, to yield bicyclo(2,2,1)heptane (XIII), which was identified by comparison of its infrared spectrum with that of an authentic sample. This established the structure as a bicyclo(2,2,1) carbon skeleton with two double bonds. The only possible structure having two double bonds in a carbon skeleton of (2,2,1) structure is the proposed one: bicyclo-(2,2,1)-2,5-heptadiene, inasmuch as any other positioning of the double bonds would lead to a double bond at a bridgehead, which violates Bredt's Rule. Another conceivable structure is XVII, but it is not clear at this point whether



XVII

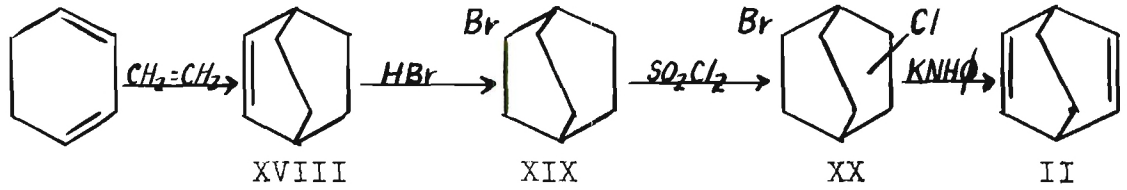
this is really an isomer or merely another resonance structure of (I), as discussed on page 4. The results of the hydrogenation together with the analysis are considered to be sufficient proof of structure.

The ultraviolet and infrared spectra are given in the appendix.

Bicyclo(2,2,1)-2,5-heptadiene was also successfully prepared by the potassium t-butoxide dehydrohalogenation of 2-chlorobicyclo(2,2,1)-5-heptene (X) at elevated temperatures, after a previous failure to effect reaction at the temperature of refluxing t-butyl alcohol. This product was shown by comparison of infrared spectra to be identical with that produced from 2,3-dichlorobicyclo(2,2,1)-5-heptene, described above; and the two samples were combined.

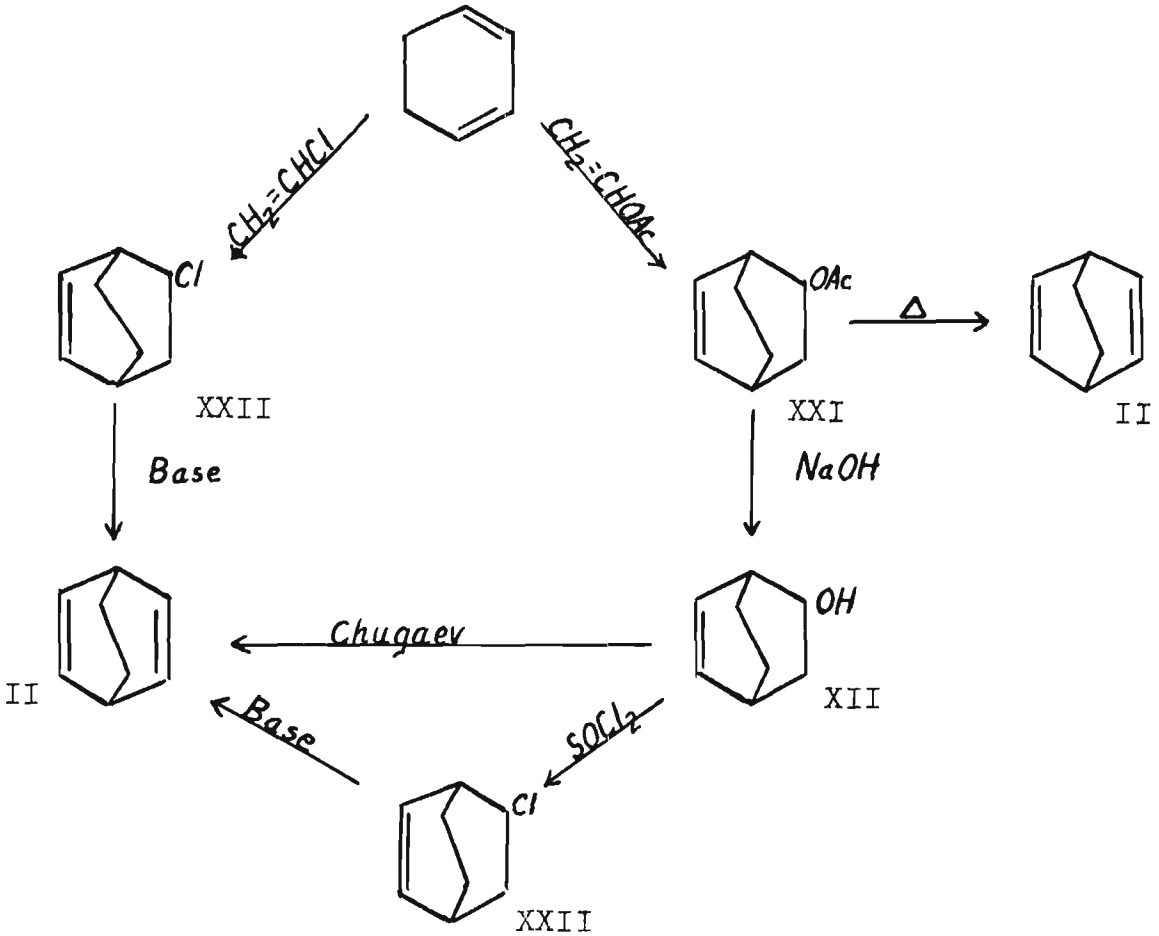
Full experimental details are given in Chapter III.

Bicyclo(2,2,2)-2,5-octadiene.—Bicyclo(2,2,2)-2,5-octadiene has been prepared in this laboratory by means of the following series of reactions:



XVIII XIX XX II

Earlier attempts involving the acetate, alcohol, and chloride as outlined below were not successful.



As in the case of bicyclo(2,2,1)-2,5-heptadiene, it was desired to use conditions and reagents mild enough to avoid decomposition to starting materials. However, in all cases it was found necessary to use rather drastic conditions in the final steps of the syntheses, and even the method which finally succeeded gave rather poor yields.

In view of the successful dehydrohalogenation of 2-chlorobicyclo(2,2,1)-5-heptene to give bicyclo(2,2,1)-2,5-heptadiene, an attempt was made to use an analogous method in the preparation of bicyclo(2,2,2)-2,5-octadiene. However, an attempt to form (XXII) by the reaction of vinyl chloride and 1,3-cyclohexadiene failed, yielding only unidentified decomposition products. The ester (XXI) and the alcohol (XII) were successfully formed, using the method of Alder (3). Treatment of (XII) with thionyl chloride (or phosphorus pentachloride) failed to give (XXII), but instead gave a product which is thought to be a rearranged chloride. Chugaev treatment of the alcohol (XII) resulted in the formation of a xanthate, but the pyrolysis gave only benzene as a distillate. The apparatus was not constructed to catch gases; so ethylene, which was presumably formed too, was not detected. An attempt to pyrolyze the ester (XXI) gave only benzene, water, and acetic acid as liquid products. Again, gases were not caught. An attempt by another member of this team to prepare 2,3-dichlorobicyclo(2,2,2)-5-octene

in a pure form also failed (17).

The successful synthesis of bicyclo(2,2,2)-2,5-octadiene was carried out jointly by Hine, Zalkow, and the writer, working as a team, and was later carried out individually by each of us.

Inasmuch as 1,3-cyclohexadiene, the starting material, is not available commercially except in small quantities at a prohibitive price, it was necessary first to develop a convenient method for preparing this compound in fairly large quantities. This was accomplished by treating the readily-available material, cyclohexene, with bromine to form cyclohexene dibromide, then subjecting the dibromide to the dehydrohalogenating action of sodium hydroxide dissolved in ethylene glycol at a temperature of around 200°. This procedure gave a material which, according to our interpretation of the infrared spectra, was approximately 80 per cent 1,3-cyclohexadiene, with the principal impurities being the difficultly-separable materials, benzene and cyclohexene. Since these compounds would not interfere in the subsequent Diels-Alder reactions, it was not felt to be worth while to purify the diene further.

Bicyclo(2,2,2)-2-octene (XVIII) was prepared by heating 1,3-cyclohexadiene with ethylene gas at a temperature of around 200° and a pressure of 1500 p. s. i. in a sealed

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(17) L. H. Zalkow, Private Communication.

reaction vessel for forty-eight hours. Following the method of Doering and Farber (15), this octene was then treated with dry hydrogen bromide in diethyl ether solution at dry-ice temperatures for several hours (until the hydrogen bromide tank had lost slightly more than the stoichiometric weight). The bromide (XIX) thus formed was chlorinated with sulfuryl chloride in carbon tetrachloride solution to yield a mixture of isomers of chloro-2-bromobicyclo(2,2,2)octane and, presumably, various dichlorides and polychlorides.

The monochlorides were separated from the more highly chlorinated compounds by fractional distillation and used in the next step without further separation. This use of a mixture could not lead to any hydrocarbon isomers after dehydrohalogenation because the only monochloride isomers capable of losing two molecules of hydrogen halide are those isomers with the chlorine atom in the 5, 6, 7, or 8 position, designating the position of the bromine atom as position 2. All these isomers would, upon dehydrohalogenation, lead to the same compound, bicyclo(2,2,2)-2,5-octadiene. Any isomers with the chlorine atom in some other position could not undergo both dehydrochlorination and dehydrobromination because such an occurrence would result in a double bond at a bridgehead (a violation of Bredt's Rule) or in an acetylenic bond in one bridge (an impossibility in small rings).

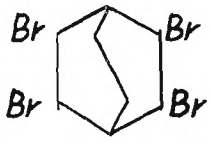
Dehydrohalogenation of the mixture of chlorobromides was accomplished by dropping the chlorobromides (dissolved in

aniline) into a solution of potassium anilide in refluxing aniline, the products distilling off as they were formed. In addition to the desired diene, considerable quantities of benzene and ethylene were also formed, presumably in a competing decomposition process of some halo compound. Benzene and ethylene can be formed from the pyrolysis of bicyclo(2,2,2)-2,5-octadiene, but this pyrolysis has not been found to take place at a very rapid rate under the stated conditions, occurring readily only upon distillation of the diene over a red-hot wire.

The bicyclo(2,2,2)-2,5-octadiene (V) thus formed was found, after purification, to be a mobile, water-white liquid boiling at 126°, with an index of refraction of 1.4912 at 24°, a density of 0.9171 at 32°, and an observed molecular refractivity of 33.63, as compared to a value of 33.81 calculated from structure (II). A carbon-hydrogen analysis indicated a formula of C_8H_{10}, in agreement with the assigned structure.

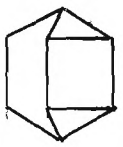
A sample of the compound hydrogenated in ethanolic solution in the presence of Adams' platinum catalyst was found to absorb two moles of hydrogen per mole of hydrocarbon to yield bicyclo(2,2,2)octane (XIV), identified by comparison of the infrared spectrum of the product with that of an authentic sample. This established the structure as a bicyclo(2,2,2) carbon skeleton with two double bonds. Further evidence for this structure is the composition of the

bromination product, whose analysis indicates a formula of $C_8H_{10}Br_4$, as would be expected from a structure of (XXIII).



XXIII

As in the case of bicyclo(2,2,1)-2,5-heptadiene, the only possible structure having two double bonds in a carbon skeleton of bicyclo(2,2,2) structure is the proposed one: bicyclo(2,2,2)-2,5-octadiene (II), inasmuch as any other positioning of the double bonds would lead to a double bond at a bridgehead, a violation of Bredt's Rule. Again, as in the previous case, another conceivable structure is (VI),



VI

but it is not clear at this point whether this is really an isomer or merely another resonance structure of (II).

Further evidence for the structure proposed is the pyrolysis of the product over a red-hot wire to give benzene and ethylene. It is difficult to see just how these products could be formed from structure (VI) unless one postulates an initial conversion to (II); the formation of benzene and ethylene from (II) is merely the reverse of the hypothetical diene addition which can be written between benzene and ethylene.

The ultraviolet and infrared absorption spectra are given in the appendices and full experimental details are given in Chapter III.

Ultraviolet absorption spectra.—Although the writer's assignment and interest were confined to synthesis, the purpose of this whole project was to study the possible interaction of the double bonds in these systems. Thus, a comment on the spectra may be in order at this point.

The ultraviolet absorption spectrum of bicyclo(2,2,1)-2-heptene shows a strong absorption beginning at about 240 millimicrons and increasing steadily as far down as the limit of our instrument (a Beckman model DU). Bicyclo(2,2,1)-2,5-heptadiene shows this same absorption, and, in addition, another absorption which shows up as a shoulder on the first absorption from about 260 to 230 millimicrons. If the two double bonds in the diene were effectively isolated from one another, this compound should be expected to absorb much as does the heptene, though perhaps more strongly. On the other hand, if they possessed interaction in the conjugation sense, a new absorption might be expected at a longer wavelength—as is the case.

The same situation is true of bicyclo(2,2,2)-2-octene and bicyclo(2,2,2)-2,5-octadiene, the octene having no appreciable absorption above 215 millimicrons, and the octadiene having a strong absorption beginning at about 260 millimicrons and increasing to the limit of our instrument. The same arguments about interaction apply to the octadiene as to the heptadiene.

All these spectra are given in the appendix.

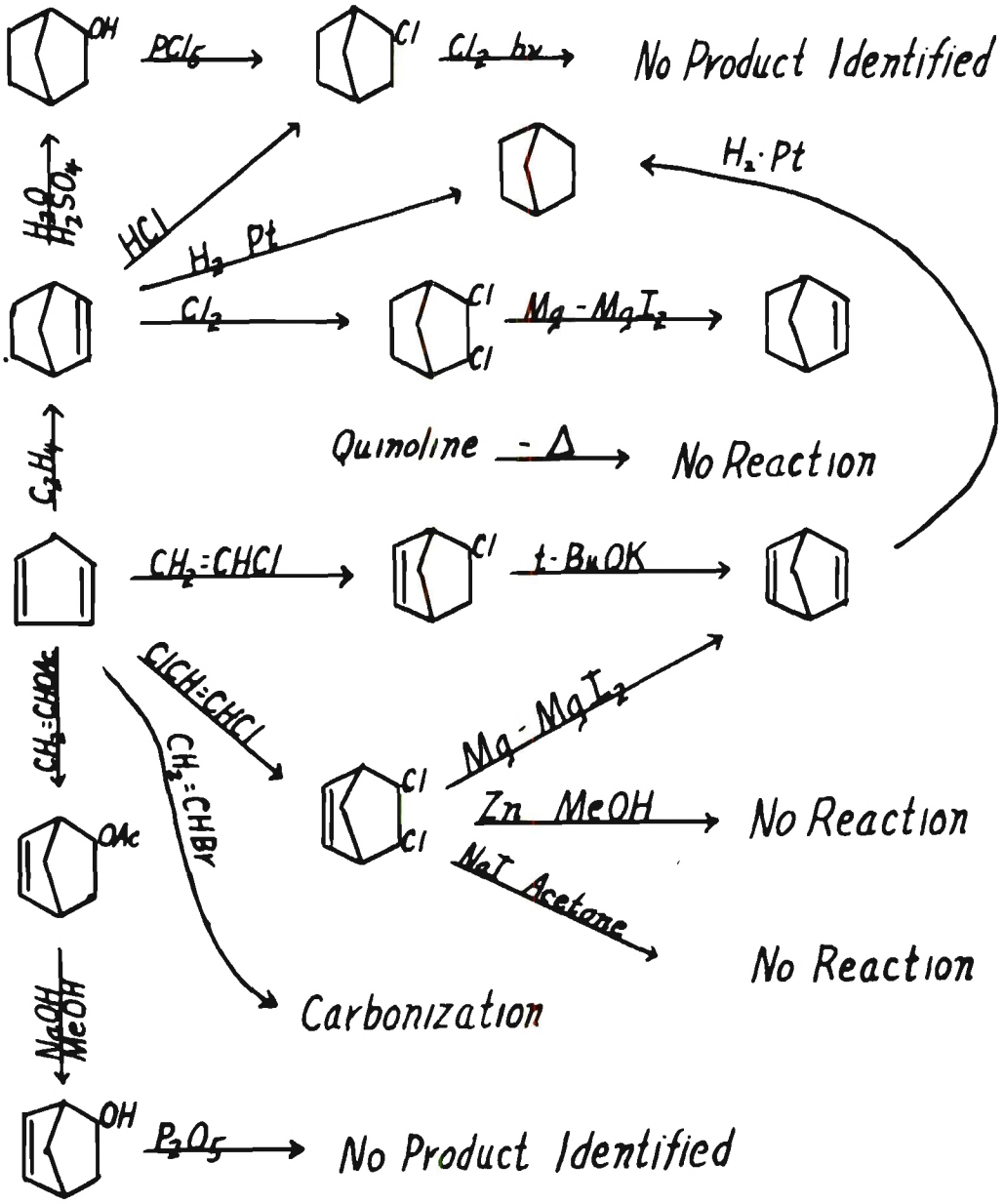
CHAPTER III

EXPERIMENTAL

CHAPTER III

BICYCLO(2,2,1)-2,5-HEPTADIENE

Reaction summary.—



Experimental Details

Preparation of norbornylene.—Technical dicyclopentadiene labeled "Matheson, 85%" was purified by distillation under a pressure of 50 mm. in a Claisen distillation flask fitted with a capillary air bubbler to prevent bumping. That fraction boiling between 88° and 89° was taken as the purified product and was stored in a refrigerator, where it solidified.

Using an adaptation of the method of Thomas (6), 1.78 moles (117 g., 125 ml.) of distilled dicyclopentadiene was placed in a 400-ml. high-pressure hydrogenation apparatus with no liner and the apparatus charged with ethylene gas to a pressure of 810 p. s. i., the maximum attainable with the ethylene tank on hand. The apparatus was heated to a temperature of 182° and held there for a period of four hours, during which time the pressure rose to a maximum of 2300 p. s. i. At the end of the heating, the pressure had fallen to 700 p. s. i.

After cooling overnight, the apparatus was opened and the contents fractionated through a 36-inch packed column at atmospheric pressure, that portion of the distillate which solidified in the take-off head being retained as the final product. Seventy-five grams of white, waxy norbornylene was obtained; this represents a yield of 45 per cent of theoretical, based on dicyclopentadiene.

This procedure was repeated a number of times with essentially the same results, and the products of all the runs were combined.

Preparation of norborneol.—A solution of 75 g. (0.8 moles) of norbornylene in 45 ml. of cyclohexane (from which the unsaturates had previously been removed with concentrated sulfuric acid) was refluxed with a solution of 33 per cent, by weight, aqueous sulfuric acid for 15 hours at a temperature of 83°. Two layers resulted, a dark-colored oil layer and a lighter aqueous layer. These were separated after cooling to room temperature. The aqueous layer was extracted once with ether, the extract combined with the oil layer, and the combined solution washed successively with water, aqueous sodium carbonate solution, and water again. The washed solution was dried for a short time over ignited calcium sulfate and then distilled through an 18-inch packed column, all distillate solidifying in the take-off head being retained as final product. Forty-seven grams of white, waxy norborneol boiling at 175-180° was obtained; this represents a yield of 52.5 per cent of theoretical, based on norbornylene.

Preparation of norbornyl chloride.—Following the procedure of Alder (3) and Komppa (5), 40 g. (0.357 moles) of norborneol was dissolved in 150 ml. of technical ligroin and cooled to approximately 0° in an ice-water bath. To this, 66.5 g. of phosphorus pentachloride was added, with stirring, as fast as the resulting effervescence would allow, and the resulting solution allowed to stand overnight to room temperature.

The next morning the resulting dark liquid was washed three times with ice-water, once with aqueous sodium bicarbonate solution, and twice more with ice-water. This left an almost water-white liquid which was dried over ignited calcium sulfate and then distilled in a Claisen apparatus. After removal of the ligroin at atmospheric pressure, during which time the flask temperature rose to 150°, the vacuum from a water aspirator was applied and 35 g. of colorless norbornyl chloride distilled at a temperature of 100°. The pressure was not measured, but was probably in the neighborhood of 20-30 mm. The yield was 75 per cent of theoretical, based on norborneol.

An alternate preparation of norbornyl chloride was carried out by hydrochlorination of norbornylene, after the method of Schmerling (9). Twenty-five grams of norbornylene dissolved in 60 ml. of olefin-free ligroin was cooled to dry-ice temperatures and kept saturated with gaseous hydrogen chloride for one hour. The resulting solution was distilled exactly as above, and with the same results. Comparison of the infrared spectra of the two products showed them to be identical, and they were combined. No data were collected on the yield of this second preparation.

Hydrogenation of norbornylene.—A solution of 14.6 g. (0.152 moles) of norbornylene in 100 ml. of 95 per cent ethyl alcohol was placed in a standard Parr hydrogenation apparatus with

0.4 grams of used Adams' platinum catalyst, and shaken with hydrogen at a starting gauge pressure of 40 p. s. i. for one hour, following the methods of Thomas (6) and Roberts (7). The resulting solution was filtered through a fritted glass filter to remove the catalyst, then subjected to separation procedures.

An attempt at direct fractionation of the alcohol solution failed due to the high vapor pressure of the solid heptane which distilled about as fast as the alcohol did, solidifying in the column head and preventing reflux. An attempt to cause recrystallization of heptane from the alcohol solution by cooling to ice temperature also failed. What remained of the alcohol solution was then diluted with a large amount of water, causing precipitation of the solute as a white, waxy, volatile solid. This solid was collected on a filter, pressed with a rubber dam, then taken up in n-pentane. A water layer separated from this solution and was removed. The resulting pentane solution was dried over ignited calcium sulfate and fractionated through an 18-inch packed column at atmospheric pressure. After the pentane was removed, a solid product began distilling at a temperature of 104.5°, necessitating heating of the take-off system with an electrical resistance wire to prevent solidification of the product. As much product as possible was removed in this manner, then a few ml. of o-xylene was added to the flask as a distillation base and a few more ml. of product was obtained.

The product, norbornylane, was a white, waxy, volatile, hygroscopic solid, melting at 88-90° and boiling at 104.5° at atmospheric pressure. The yield was not determined due to the obvious losses in the separation procedures.

Synthesis of 2-acetoxybicyclo(2,2,1)-5-heptene.—Following the method of Alder (3), 78 ml. of dicyclopentadiene (equivalent to one mole of monomer) was placed in a high-pressure reaction vessel with 130 ml. of stabilized vinyl acetate (which represented a slight excess of vinyl acetate) and a pinch of hydroquinone to inhibit polymerization. The vessel was sealed and heated to ca. 170° for approximately 20 hours, during which time the pressure rose to ca. 100 p. s. i. and then fell to a value too low to register on the 5000-pound gauge. This procedure was repeated twice and the material from all three runs was combined for fractionation.

In order to remove unreacted vinyl acetate, the combined product from the three runs described above was distilled through an 18-inch packed column at atmospheric pressure until the flask temperature reached 180°. Then the remainder was fractionated under a pressure of 50 mm. The yield was 190 g. of water-white ester boiling at 90-95° at 50 mm. representing a yield of 41.6 per cent, based on cyclopentadiene.

Preparation of 2-hydroxybicyclo(2,2,1)-5-heptene.—Again following the method of Alder (3), 188 g. (1.24 moles) of 2-acetoxybicyclo(2,2,1)-5-heptene was refluxed for one hour in an 18-inch fractionating column with 60 g. of sodium hydroxide in a solution of 750 ml. of methanol and 150 ml. of water. The take-off valve was then opened and 500 ml. of methanol allowed to distill. The residue was poured into water and the resulting solution extracted with two 125-ml. portions of diethyl ether. The extract was then dried over calcium chloride and evaporated under vacuum, first at room temperature and then with gentle heating. As the evaporation proceeded, the solution gradually thickened into a viscous syrup but could not be induced to form any crystals. Finally, as the last of the solvent evaporated, the entire mass solidified, giving 68 g. of dirty yellow crystals; this represents a yield of 50 per cent of crude alcohol, based on ester.

A small sample of crude alcohol was recrystallized (with considerable difficulty) from petroleum ether, and found to melt at 95-100°.

Attempted dehydration of 2-hydroxybicyclo(2,2,1)-5-heptene.—Using a method similar to that which Alder used to dehydrate 2-hydroxybicyclo(2,2,1)heptane to bicyclo(2,2,1)-2-heptene (norbornylene) (3), 7 g. of 2-hydroxybicyclo(2,2,1)-5-heptene was dissolved in cold pentane and poured onto solid phosphorus

pentoxide contained in a reflux apparatus. A vigorous reaction ensued, giving off enough heat to reflux the pentane for several minutes. After this reaction subsided, the pentane layer was poured off and the solid residue dissolved in water. The aqueous layer was extracted once with fresh pentane and the extract combined with the original pentane layer along with 10 ml. of o-xylene for fractional distillation. Fractionation through an 18-inch packed column yielded only pentane and o-xylene.

In another attempt, 60 g. of crude alcohol was dissolved in 100 ml. of o-xylene and added, with stirring, to 43 g. of phosphorus pentoxide suspended in 250 ml. of o-xylene at room temperature. There was no apparent reaction. Heating was begun and carried to reflux (which occurred at a liquid temperature of 145°) with no indication of reaction except a gradual darkening of the solution. Fractional distillation of the xylene layer yielded only xylene, with no low-boiling component.

Preparation of 2,3-dichlorobicyclo(2,2,1)-5-heptene.—Following the method of Alder (3), 145 g. (2.20 moles) of monomeric cyclopentadiene was heated with 426 g. (4.4 moles) of stabilized trans-dichloroethylene in a high-pressure reaction vessel for three and one-half hours, the temperature reaching a maximum of 160°, after which it was allowed to cool overnight. The resulting product was fractionated through an 18-inch

packed column at atmospheric pressure to remove unreacted trans-dichloroethylene, and then the residue was fractionated under a pressure of 56 mm. One hundred thirty-two and one-half grams of water-white oil boiling at 85-90° was obtained, representing a yield of 37 per cent, based on cyclopentadiene.

Attempted dehalogenation of 2,3-dichlorobicyclo(2,2,1)-5-heptene.—Thirty ml. of the dichloro compound was dissolved in 80 ml. of dry methanol and refluxed with 16 g. of zinc dust overnight. The remaining zinc was then filtered off and the liquid distilled at atmospheric pressure. No distillate was obtained except methanol; the flask residue was not investigated.

In another attempt, 7.5 ml. of the dichloro compound was added to 14 g. of sodium iodide dissolved in refluxing acetone, refluxed for three hours, then allowed to stand for several days. No sodium chloride was precipitated, and there was no apparent reaction of any kind.

Preparation of magnesium-magnesium iodide dehalogenating reagent.—Following the procedure of Summerbell and Umhoefer (8), a dehalogenating reagent was prepared by adding, in small portions over a period of several hours, 89 g. (0.7 moles) of iodine to a suspension of 24.3 g. (1 mole) of magnesium metal in 500 ml. of dry n-butyl ether in a flask equipped with a reflux condenser and a mechanical stirrer. Completion of this addition resulted in a black suspension of magnesium iodide

and magnesium metal in refluxing n-butyl ether. This mixture is reported to be a powerful dechlorinating agent even under mild conditions (8).

Preparation of norbornylene dichloride.—Ninety-four grams (1 mole) of norbornylene was dissolved in 100 ml. of carbon tetrachloride, placed in a tall, slender reaction flask fitted with a gas-dispersal tube, and cooled in an ice-water bath. Elemental chlorine was passed in through the dispersal tube at such a rate as to maintain the temperature in the neighborhood of 25° until the reaction mixture had gained 70 g. This required about eight hours.

The reaction mixture was then fractionally distilled under a pressure of 50 mm. yielding 46 g. of norbornylene dichloride, b. p. 89-93°, representing a yield of 27.9 per cent, based on norbornylene.

Dechlorination of norbornylene dichloride.—Using a method modeled on that of Summerbell and Umhoefer (8), the dechlorinating reagent prepared as described above was allowed to cool to just below reflux temperature and 33 g. of norbornylene dichloride added dropwise. A vigorous reaction occurred during the addition but was easily controlled by controlling the dropping rate of norbornylene dichloride. After addition was complete, the mixture was allowed to cool to room temperature, filtered to remove magnesium and other solids, and the filtrate fractionated

through a 14-inch packed column. About 5 ml. of product with the odor of norbornylene, boiling at 100° and solidifying in the receiver, was obtained.

Dechlorination of 2,3-dichlorobicyclo(2,2,1)-5-heptene.—A magnesium-magnesium iodide mixture in n-butyl ether was prepared as described above; and 30 g. (0.19 moles) of 2,3-dichlorobicyclo(2,2,1)-5-heptene was added dropwise, with stirring, keeping the temperature of the dehalogenating reagent just below reflux. A vigorous reaction ensued which was moderated by limiting the addition rate of the dichloride. The total mixture was refluxed for one-half hour after addition was complete, then decanted and the liquid fractionated through a 14-inch packed column. Four ml. (3.6 g.) of bicyclo(2,2,1)-2,5-heptadiene, a water-white, mobile liquid boiling at 89.5° at atmospheric pressure and with an odor reminiscent of norbornylene (but distinguishable from that of norbornylene) was obtained. This represents a yield of 20.5 per cent, based on the dichloro compound. Another, larger, run gave a yield of 16 ml., which represented a yield of 19.2 per cent, based on the dichloro compound.

This material was found to have a refractive index of 1.467 and a density of 0.8992 at 26°. A carbon-hydrogen analysis by Clark Microanalytical Laboratory gave the following

results:

	Calc.	Found
Carbon	91.25	91.20
Hydrogen	8.75	8.95

in good agreement with the assigned formula of C_7H_8.

Preparation of 2-chlorobicyclo(2,2,1)-5-heptene.—A glass liner, built to fit inside a high-pressure reaction vessel, was cooled in a dry-ice bath, 66 g. (one mole of monomer) of dicyclopentadiene added, and the whole allowed to cool to dry-ice temperature. Sixty-five grams (excess) of vinyl chloride was distilled into the liner directly from the tank and a pinch of hydroquinone added to inhibit polymerization of the vinyl chloride. The glass liner was then placed in the high-pressure vessel, the vessel sealed, and heated to 180° overnight. The product, a dark brown oil, was fractionally distilled through a 14-inch packed column under vacuum. That portion boiling at 78-80° at a pressure of 55 mm. was retained as the product. This synthesis was performed only once, and the yield was not recorded.

This product has been reported previously by Alder (3).

Attempted dehydrohalogenation of 2-chlorobicyclo(2,2,1)-5-heptene.—Based on the method of Alder, who dehydrohalogenated 2-chlorobicyclo(2,2,1)heptane to norbornylene (11), 100 ml. of freshly-distilled quinoline (boiling above 230°) was heated to 110° and a sample of the chloro compound added dropwise.

There was no apparent reaction, so the temperature was gradually raised to reflux while the slow addition of the chloro compound continued. No reaction was detected.

Dehydrohalogenation of 2-chlorobicyclo(2,2,1)-5-heptene.—A solution of potassium t-butoxide was prepared by dissolving 19.5 g. of potassium metal in 300 ml. of t-butyl alcohol and warmed to just under reflux temperature. Thirty grams (0.233 moles) of 2-chlorobicyclo(2,2,1)-5-heptene was added slowly through a dropping funnel. No potassium chloride precipitate formed. There was no sign of any reaction except a darkening of the solution as heating was continued. The solution was refluxed for an hour, then allowed to stand at room temperature for a week. At the end of this time there was still no sign of any reaction. Nevertheless, the solution was placed under a 14-inch packed column and slowly distilled at atmospheric pressure.

The first 180 ml. of distillate boiled at 80°, and had the odor of t-butyl alcohol. After this, an odor similar to that of bicyclo(2,2,1)heptadiene prepared above became apparent, although the distillation temperature had not changed. By this time, considerable solid t-butoxide had formed in the flask and the flask temperature was much higher than previously. Another 40 ml. of distillate was collected before distillation ceased due to dryness in the flask. This last 40 ml., collected at 75-80°, was diluted with a large amount of water and two layers formed. The upper (oil) layer was removed,

dried over calcium chloride, mixed with o-xylene for a distillation base, and fractionated through a 14-inch packed column. About 6 ml. of liquid boiling at 89.5° was collected. Comparison of infrared spectra showed this material to be identical with the sample of bicyclo(2,2,1)-2,5-heptadiene described previously. This represents a yield of 25 per cent.

Preparation of vinyl bromide[1].—A solution of 80 g. of potassium hydroxide in 500 ml. of absolute ethanol was placed in a two-liter flask equipped with a stirrer and a reflux condenser, and warmed to 60°. Four hundred grams of ethylene dibromide was added slowly through a dropping funnel; a vigorous reaction ensued, accompanied by precipitation of potassium bromide and evolution of gaseous vinyl bromide. The vinyl bromide was led from the top of a reflux condenser (which served to return most of the entrained ethanol) into a dry-ice trap where it condensed to a liquid. The total yield of crude vinyl bromide was 130 g. (38 per cent based on ethylene dibromide).

No attempt was made to purify the product any further, since any contaminating alcohol would not be harmful in the next step, and it was felt that the additional purity would not compensate for the purification losses of vinyl bromide.

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[1] This preparation was based on general directions given to the writer by W. H. Brader, of this laboratory, (18).

(18) W. H. Brader, Private Communication.

Combination of cyclopentadiene and vinyl bromide.—Sixty-six grams of dicyclopentadiene and 125 g. of crude vinyl bromide were placed in a high-pressure reaction vessel which had been chilled in the freezing compartment of a refrigerator, sealed, and heated to 180° overnight.

Extensive carbonization and polymerization occurred. No liquid product was found at all, only black stringy solid. This solid was hard and brittle and soluble in benzene and similar solvents. When plasticized with nitrobenzene, it formed a rubbery plastic gel. It was thought to be largely polyvinyl bromide, liberally mixed with carbon, and was not investigated further. The experiment was not repeated.[1]

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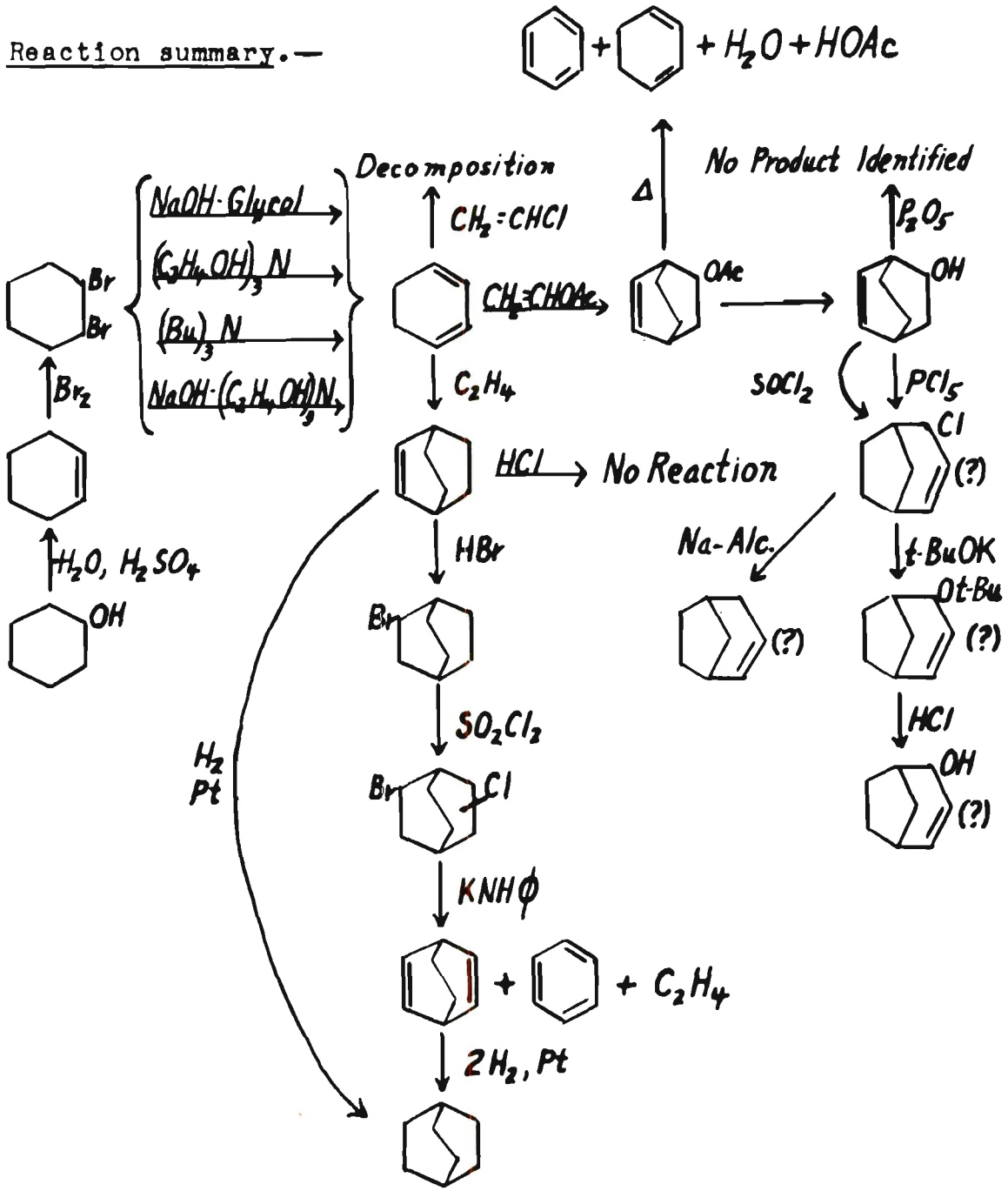
[1]Roberts, et al., report that they have carried out this condensation successfully by heating cyclopentadiene and vinyl bromide in a sealed glass vessel to 165° overnight. They report that the same procedure in a steel vessel resulted in the formation of considerable amounts of nortricyclyl bromide, (19).

(19) J. D. Roberts, E. R. Trumbell, Jr., W. Bennett, and R. Armstrong, J. Am. Chem. Soc., 72, 3116 (1950).

BICYCLO(2,2,2)-2,5-OCTADIENE

Reaction summary.—



Experimental Details

Preparation of cyclohexene.—Most of the cyclohexene used in this work was a commercial product, but some of it was prepared here by the dehydration of commercial cyclohexanol with concentrated sulfuric acid, according to the procedure given in Organic Syntheses (20).

Preparation of cyclohexene dibromide[1].—Five moles of cyclohexene was placed in a 2-liter, 3-necked flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer dipping into the liquid, and a dry-ice-acetone cooling bath. Five moles of bromine was added through the dropping funnel at such a rate as to maintain the temperature of the liquid around 5°, the addition requiring about two hours. A very slight excess of bromine was used, resulting in a red solution, and fresh cyclohexene was then added dropwise until the red color faded. The cyclohexene dibromide thus obtained, a colorless, fuming liquid, was used within the hour without purification.

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[1]This preparation is an adaptation of the Organic Syntheses method wherein bromine is added to a solution of cyclohexene in carbon tetrachloride cooled by an ice-salt bath (21). Our method is a great deal faster and gives a product equally pure.

(20) Organic Syntheses, edited by H. Gilman and A. H. Blatt, New York: John Wiley and Sons, Inc., Second edition, 1951, Collective Volume I, p. 183.

(21) Organic Syntheses, edited by A. H. Blatt, New York: John Wiley and Sons, Inc., 1950, Collective Volume II, p. 171.

Preparation of 1,3-cyclohexadiene.—Four different alkaline media were tried in this reaction. In each case, the dibromide was added to the base which was maintained at a temperature near 200°, and the product removed continuously by distillation.

Tri-n-butylamine Eight hundred seventy-five grams of tri-n-butylamine was heated to 203° and 1.7 moles (412 g.) of dibromide added, slowly, with stirring. Distillation of product was continuous, about 750 ml. of distillate being collected. This was fractionated through a 14-inch packed column, and 115 ml. of product boiling at 80° was obtained. The refractive index suggested this to be around 50 per cent 1,3-cyclohexadiene.[1] A repeat run gave substantially the same results.

Triethanolamine The above procedure was repeated, substituting triethanolamine for tri-n-butylamine. Results were generally poorer, the process yielding smaller amounts of even less pure material.

NaOH in triethanolamine Six moles of NaOH was dissolved in one liter of triethanolamine at 165°, and three moles of cyclohexene dibromide added slowly with continuous distillation of product. This product was in two phases, a

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[1]Not much reliance should be placed in these values, since the material contained at least three major components, all of different refractive index; and no careful study of the system was ever made.

water phase and an oil phase. After removal of the water phase, the hydrocarbon phase was dried over calcium chloride and fractionated through a 14-inch packed column. Eighty ml. of product boiling at 80° was obtained, and refractive index data suggested a 1,3-cyclohexadiene purity of 80 or 90 per cent.[1]

NaOH in ethylene glycol Twelve moles of NaOH was dissolved in one liter of ethylene glycol at an elevated temperature, and the solution was then distilled (removing water) until the liquid temperature reached 200°. Five moles of cyclohexene dibromide was then added slowly, with stirring, and the product distilled continuously. This product consisted of two phases. The water-miscible phase was removed, and the hydrocarbon phase dried over calcium chloride and fractionated. One hundred fifty ml. of material boiling at 80° and with a refractive index suggesting a purity of 70 to 80 per cent was obtained.[1]

This method has since been developed further by Hine, Zalkow, and Gardner, of this laboratory, and has been employed to prepare large quantities of diene of 80 per cent purity or better.

In the work done by this writer, each of these processes gives a first distillate which, upon refractionation,

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[1] Not much reliance should be placed in these values, since the material contained at least three major components, all of different refractive index; and no careful study of the system was ever made.

is found to contain 20-50 per cent of high-boiling material. This material, when heated with fresh NaOH in glycol, is found to give a further yield of 1,3-cyclohexadiene in the same manner as the original dibromide.

Most of the 1,3-cyclohexadiene which the writer used was actually prepared by other members of this team.

Preparation of bicyclo(2,2,2)-2-octene.—This procedure was first employed in this laboratory by the writer. It was greatly improved by Mr. Leon Zalkow, and many of the subsequent runs were performed jointly by us. The following description is of a typical run.

Four hundred fifty ml. (4.5 moles) of 1,3-cyclohexadiene was placed in a high-pressure reaction vessel of approximately 1500 ml. capacity, and the vessel and contents were cooled to 0° in an ice-water bath. Gaseous ethylene was then charged into the vessel from a tank to a pressure of 550 p. s. i. (the tank pressure). During this time, the vessel was not shaken. Heating was begun and continued for forty hours at a temperature of 197°, during which time the pressure rose to a maximum of 1500 p. s. i. and then fell slowly as the reaction proceeded.

Separation of products was effected by fractional distillation at atmospheric pressure, that portion which boiled at $132.0\text{-}132.5^{\circ}$ and solidified in the receiver being taken as bicyclo(2,2,2)-2-octene. The material was a white,

waxy solid, with a camphor-like odor and a melting range of 99-105°. A subsequent sample, more carefully purified, had a melting range of 99-101°. The melting point of bicyclo(2,2,2)-2-octene as prepared by other methods is variously given in the literature as 113-114° (4) and 141-144° (22).[1] Nevertheless, in view of the method of preparation, and in view of the successful use of this product in further synthesis, it is felt that this product is the correct one.

One hundred sixty-two grams of product were obtained, representing a yield of 33.3 per cent, based on cyclohexadiene. The writer understands that still further refinements by Mr. Zalkow have since produced yields on the order of 60 per cent.

Preparation of bicyclo(2,2,2)octane.—A sample of bicyclo-(2,2,2)-2-octene weighing 5.268 g. was dissolved in 75 ml. of 95 per cent ethanol, and hydrogenated in a manner identical to that already described for bicyclo(2,2,1)-2-heptene. The material was found to absorb one mole of hydrogen per 108 g. (one mole) of sample and to yield a white, waxy product which

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[1] L. H. Zalkow, of this laboratory, reports a melting point of 110-113° for material prepared by him (17). It should also be noted that Doering, et al., may have meant to say 111-114°, since they quote Seka and Tramposch as reporting 143-144° instead of 113-114° as they actually reported.

(22) W. von E. Doering, M. Farber and A. Sayigh, J. Am. Chem. Soc., 74, 4370 (1952).

melted, after purification by resublimation, at 168-169°. This corresponds to that reported for bicyclo(2,2,2)octane in the literature by Alder (169-170°) (23), Komppa (168°) (5), and Bartlett (168-169°) (24). This material was desired only as a reference, therefore the product was not weighed.

Preparation of 2-bromobicyclo(2,2,2)octane.—Following the method of Doering and Farber (17), 99 g. (0.92 moles) of bicyclo(2,2,2)-2-octene was dissolved in 150 ml. of diethyl ether and cooled to dry-ice temperature. Dry hydrogen bromide was passed into the vapor space above the liquid and refluxed with the solution using a dry-ice-cooled reflux condenser until the hydrogen bromide tank had lost slightly more than 98 g. The apparatus was then left in the hood to warm to room temperature overnight. The next day the resulting light amber, fuming solution was distilled through a 27-plate column at atmospheric pressure until the flask temperature reached 140° in order to remove ether and any unreacted octene. Distillation was continued under vacuum and 149 g. of white waxy bromide were obtained, boiling at

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(23) K. Alder, G. Stein, F. v. Buddenbrock, W. Eckardt, W. Frercks, and St. Schneider, Ann., 514, 1 (1934).

(24) P. D. Bartlett and G. F. Woods, J. Am. Chem. Soc., 62, 2933 (1940).

120-121° at 52 mm., and representing a yield of 86 per cent based on octene.

Preparation of chloro-2-bromobicyclo(2,2,2)octane.—Following the methods of Roberts (7) and Zalkow (17), 149 g. of 2-bromobicyclo(2,2,2)octane was dissolved in 150 ml. of carbon tetrachloride, and 130 ml. of sulfuryl chloride was cautiously added with stirring. A moderate reaction occurred, with evolution of hydrogen chloride gas, but this soon stopped. A pinch of benzoyl peroxide was added to catalyze the reaction and the solution was refluxed under moderate heating overnight in the hood. After cooling and standing for 24 hours, the resulting solution was fractionated through a 27-plate column, first at atmospheric pressure, then under a vacuum. One hundred twenty-six grams of white, waxy product was obtained, boiling from 108-155° at 34 mm. This was considered to be a mixture of isomers of the chlorobromide, and no attempt was made to separate them.

Preparation of bicyclo(2,2,2)-2,5-octadiene.—

Preparation of dehydrohalogenating reagent Following the method developed by Hine in this project (25), 60 g. of metallic potassium was dissolved with stirring in 360 ml. of refluxing distilled aniline over a period of about three hours.

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(25) Jack Hine, Private Communication.

A short column was then attached and the solution distilled until the head temperature reached 175°. The solution was then allowed to cool to 125°, at which temperature it was maintained.

Addition of chlorobromides A solution was made of 126 g. of the above-mentioned chlorobromides in aniline and added dropwise, with stirring, to the above-described reagent. A sealed apparatus was used, with a water displacement gas collector attached, and the temperature controlled very carefully. The reaction was exothermic, and it was found necessary to hold the dropping rate to a very low value in order not to exceed 125°, at which temperature evolution of gas occurred. The addition required about three hours.

Several other runs have been made, adding the chlorobromide solution at reflux. This procedure seemed to give larger amounts of gas and smaller yields of diene; but no conclusive results are available at present and work is continuing by other workers.

Separation of products The above solution was allowed to cool overnight; then the reaction flask was transferred to a 27-plate column and heated to 110°. A vacuum sufficient to make the solution boil at this temperature was applied, and the solution distilled, the vacuum being regulated continually so as to keep the flask temperature from rising above 130° at

any time.[1] This required a pressure on the order of 140 mm. Approximately 5 ml. of benzene was obtained; followed by about 15 ml. of benzene, octadiene, and octene[2]; followed by aniline, octadiene, and octene.[2] All of these products with the exception of the octene were identified without separation by means of their infrared spectra.[2]

Five ml. of the aniline containing fraction was extracted with concentrated hydrochloric acid to remove aniline, and the resulting hydrocarbon residue was combined with the benzene-octadiene fraction for further fractionation. This fractionation was carried out using a very small tantalum wire spiral column. About three ml. of benzene was obtained first and discarded, followed by about three ml. of a liquid fraction boiling from 126-130°, followed by a fraction boiling at 130°, which later solidified.

The fraction boiling from 126-130° was determined by means of infrared spectra to be identical with bicyclo(2,2,2)-2,5-octadiene obtained from previous runs by other members of this team, with some of the solid fraction dissolved in it. A purer sample of octadiene from another run was found to boil at 126°.

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[1] The limitation of the temperature to this value was thought necessary to prevent pyrolysis of the octadiene. Octadiene has since been found to be stable under these conditions, and the temperature limitation is no longer used.

[2] Bicyclo(2,2,2)octene was not positively identified here. Its identity was inferred from its boiling point and from the probability of some 2-bromobicyclo(2,2,2)octane having been present in the chlorobromides.

This material was found to have an index of refraction of 1.4912 at 24°, and a density of 0.9171 at 32°. Carbon-hydrogen analysis by Clark Microanalytical Laboratory gave results of:

	Calc.	Found
Carbon	90.51	90.54
Hydrogen	9.49	9.54

in good agreement with the assigned structure.

Hydrogenation of bicyclo(2,2,2)-2,5-octadiene.—A micro hydrogenation apparatus was improvised by attaching a mercury manometer to a standard Parr catalytic hydrogenation apparatus operated with the reservoir tank shut off from the reaction flask, and calibrated by means of several hydrogenation runs on known pure bicyclo(2,2,2)-2-octene. Two samples of octadiene, weighing 0.0520 g. and 0.0401 g. respectively, were then hydrogenated in the same manner as the calibrating samples; both were found to absorb two moles of hydrogen for each mole of sample.

The hydrogenated alcoholic solution was then diluted with a great excess of water and the solid product thereby thrown out of solution. This product, a white, waxy solid, was filtered off, pressed between sheets of filter paper, and totally sublimed in order to dry it. The infrared spectrum showed it to be bicyclo(2,2,2)octane only.

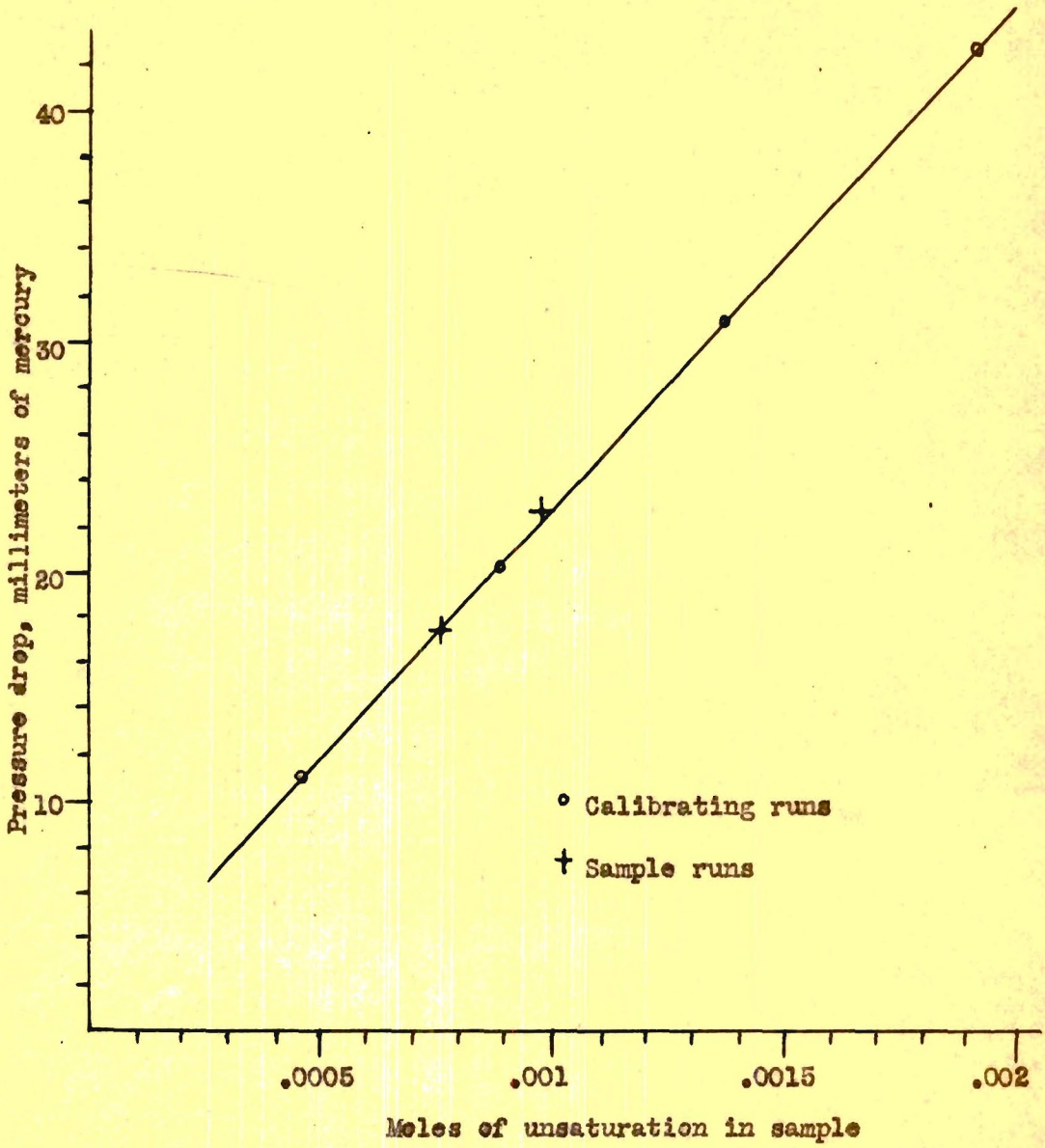

FIGURE 1. Catalytic hydrogenation of bicyclo(2,2,2)-2-octene (calibrating runs) and bicyclo(2,2,2)-2,5-octadiene (sample runs) to determine unsaturation.

Preparation of bicyclo(2,2,2)-2,5-octadiene tetrabromide.[1]—One drop of bicyclo(2,2,2)-2,5-octadiene contained in a sample vial was brominated with elemental bromine at room temperature, and the red liquid which resulted digested with ethanol. This left a crumbly solid, m. p. 92-98°. Recrystallization from ether-ethanol gave a material m. p. 101.5-102.5°, which upon recrystallization from hexane melted at 103.0-103.5°.

This final material was sent to Clark Microanalytical Laboratory for carbon-hydrogen-bromine analysis, with the following results:

	Calc.	Found	
Carbon	22.56	22.79	22.75
Hydrogen	2.37	2.49	2.52
Bromine	75.07	74.81	74.76

Combination of 1,3-cyclohexadiene with vinyl chloride.—One mole of cyclohexadiene was heated with one mole of vinyl chloride in the presence of a small amount of hydroquinone to a temperature of 250° in a sealed high-pressure reaction vessel for four days. A considerable amount of decomposition occurred during the heating, with the production of hydrogen chloride and black tarry materials. About 80 ml. of dark, greenish-brown, fluorescent liquid was obtained, but could not be resolved into any definite fractions. The experiment was not repeated.

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[1] This derivative was actually prepared twice, first by the writer, and later by Dr. Hine as a confirmation.

Preparation of 2-acetoxybicyclo(2,2,2)-5-octene.—Two hundred ml. (2.10 moles) of 1,3-cyclohexadiene was combined with 200 ml. of stabilized vinyl acetate monomer and approximately two g. of hydroquinone in a high-pressure reaction vessel and heated to a temperature of 190° for seven days. The product, a light amber, mobile liquid, was fractionated through a 14-inch packed column. This yielded 109 g. of liquid distillate boiling at 125° at a pressure of 44 mm., with a density of 1.096 at 32°, an index of refraction of 1.4980 at 24°, and having a typical ester odor. This represents a yield of 31.2 per cent, based on cyclohexadiene.

Alder and Ricker (3) have reported the preparation of this compound in "small yields" but they give no properties.

Preparation of 2-hydroxybicyclo(2,2,2)-5-octene.[1]—One hundred seventy-four grams of 2-acetoxybicyclo(2,2,2)-5-octene was dissolved in 600 ml. of methanol and combined with a solution of 50 g. of sodium hydroxide in 200 ml. of water. Two layers formed but were neither separated nor stirred since the agitation of boiling was sufficient to keep them mixed.

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[1] Since the preparation of 2-hydroxybicyclo(2,2,2)-5-octene in this laboratory, Wildman and Saunders have reported its earlier preparation by them (26). They prepared it both by saponification of 2-acetoxybicyclo(2,2,2)-5-octene, after Alder and Rickert (3) and by the lithium aluminum hydride reduction of 2-ketoxybicyclo(2,2,2)-5-octene. They showed the two samples' identity by means of infrared spectra and the p-nitrobenzoate derivative.

(26) W. C. Wildman and D. R. Saunders, J. Org. Chem., 19, 381 (1954).

This mixture was refluxed for three hours, then left to stand overnight. The next day there were still two layers: an upper layer of a dark, yellow-brown solution, and a lower layer of a whitish emulsion. The lower layer was removed and discarded, while the upper layer was fractionally distilled.

After 400 ml. of methanol was removed, the residue was poured into approximately 1.5 liters of water, whereupon a reddish oil separated. This oil was taken up in diethyl ether; the solution was dried over calcium chloride and then distilled until the flask temperature reached 130°. The remaining liquid was poured into a crystallizing dish, covered with a watch-glass, and allowed to cool, whereupon the entire mass solidified into dirty yellow crystals weighing 73 g. This represented a yield of crude alcohol of 56.5 per cent, based on ester.

After recrystallization from ligroin followed by sublimation, the white, waxy leaflets melted at 160-162°.

Attempted dehydration of 2-hydroxybicyclo(2,2,2)-5-octene.— Twenty-two grams of 2-hydroxybicyclo(2,2,2)-5-octene was sifted slowly into 14 ml. of thionyl chloride contained in an open vessel in the hood. During the addition, a vigorous reaction occurred, accompanied by the evolution of copious amounts of hydrogen chloride and the formation of a thick black solution. After being allowed to stand for one hour,

this solution was fractionally distilled through a 14-inch Vigreaux column at a pressure of 54 mm. Approximately 20 ml. of water-white liquid boiling at 106° at this pressure was obtained. Its index of refraction at 20° was 1.5160; it was shown to decolorize bromine water and permanganate; a chlorine analysis by L. H. Zalkow showed values of 23.7 and 23.8 per cent, corresponding to one chlorine atom per bicyclooctane unit. That this material was not 2-chlorobicyclo(2,2,2)-5-octene was suggested by repeated failures to induce it to be dehydrohalogenated to bicyclo(2,2,2)-2,5-octadiene. Its structure is tentatively assigned to be 2-chlorobicyclo(3,2,1)-3-octene, an isomer of the desired compound, although this structure has not as yet been proven.

Chlorination of the alcohol with phosphorus pentachloride in ligroin gave the same product.

Reactions of assumed 2-chlorobicyclo(3,2,1)-3-octene.—Forty-nine grams of assumed 2-chlorobicyclo(3,2,1)-3-octene (which at that time was thought to be 2-chlorobicyclo(2,2,2)-5-octene) was refluxed with 20 g. of metallic potassium dissolved in 440 ml. of t-butyl alcohol for 18 hours, in an attempt to dehydrohalogenate it to bicyclo(2,2,2)-2,5-octadiene. At the end of this time, the t-butyl alcohol was distilled, and the residue, which consisted of organic material boiling above 200° and potassium chloride, flooded with water. An organic layer separated, was washed with water, dried, and distilled

under water-aspirator vacuum. Approximately 25 ml. of colorless liquid boiling at 135° at an estimated 100 mm. was obtained. The high boiling point suggested an ether; an infrared spectrogram indicated the absence of an alcohol group and suggested the presence of a t-butyl group. The carbon-hydrogen analysis was consistent with the formula 2-t-butoxybicyclo(3,2,1)-3-octene, or the isomeric 2-t-butoxybicyclo(2,2,2)-5-octene. The former structure is favored in view of the surprising lability of the chlorine atom (as compared to 2-chlorobicyclo(2,2,1)-5-heptene), the failure to dehydrohalogenate, and the known tendency of these (2,2,2) systems to rearrange to (3,2,1) systems (15) (16).

In order to determine whether the carbon skeleton had, indeed, rearranged, an attempt was made to cleave the ether back to an alcohol which could be compared with the original. Accordingly, a small sample was refluxed with concentrated hydrochloric acid for six hours, then the mixture was neutralized and distilled. The distillate consisted of two layers, water and an organic liquid. The organic layer was separated, dried, and its infrared spectrum determined. The spectrum showed that this product was not identical with 2-hydroxybicyclo(2,2,2)-5-octene. The presence of a clear alcohol band was noted, and there was no indication of t-butyl alcohol or t-butyl chloride.

A small sample (approximately two ml.) of the chloro compound was refluxed with metallic sodium suspended in

isopropyl alcohol in an attempt to reduce it to the corresponding hydrocarbon. A yellow oil resulted. This oil was washed with dilute hydrochloric acid and water, then distilled in a semi-micro apparatus at atmospheric pressure. The distillate was a colorless liquid boiling in the neighborhood of 175° (there being insufficient material to establish complete equilibrium around the thermometer bulb).

None of the materials in this section were actually identified or completely characterized. Their infrared spectra are on file, and work on them is being continued by other investigators.

Pyrolysis of 2-acetoxybicyclo(2,2,2)-5-octene.—A sample of this ester was distilled at atmospheric pressure through a red-hot pyrex tube packed with glass helices. The entire distillate was condensed into one fraction which consisted of a bright yellow, mobile liquid with a sharp, musty odor. This distillate was fractionally redistilled through a 14-inch packed column and yielded two fractions. One of these was identified by means of infrared spectra as a mixture of benzene, 1,3-cyclohexadiene, and water, and the other by means of the boiling point and odor as largely acetic acid. It is conjectured that ethylene may also have been formed, but no provision was made for trapping gases, so this is not known.

At any rate, the procedure did not lead to the production of bicyclo(2,2,2)-2,5-octadiene, which was desired, and was not studied further.

Attempted hydrochlorination of bicyclo(2,2,2)-5-octene.— Following the general procedure already described for the hydrochlorination of bicyclo(2,2,1)-5-heptene, 12.5 ml. of bicyclo(2,2,2)-5-octene dissolved in 25 ml. of ligroin was treated with gaseous hydrogen chloride for nine hours at ice temperature, and the resulting solution distilled. Only unchanged octene was found. Another attempt using dry-ice temperatures also failed.

Chugaev treatment of 2-hydroxybicyclo(2,2,2)-5-octene.— Thirty-six grams of 2-hydroxybicyclo(2,2,2)-5-octene dissolved in 400 ml. of freshly-distilled decalin was stirred and heated with 11.4 g. of metallic potassium until the metal had all disappeared. Six hundred ml. of diethyl ether and 40 g. of carbon disulfide were added, and stirring continued for two more hours. After standing overnight, the solution was warmed to reflux temperature and 90 g. of methyl iodide added slowly. The resulting suspension of yellow xanthate was stirred at reflux for four hours, then distilled through a 20-cm. Vigreaux column.

After removal of excess low-boiling solvents, the distillation temperature rose sharply to 150°, and then more slowly to 180°, at which approximate temperature the remainder of the material distilled. This high-boiling fraction was washed with five portions of five per cent aqueous potassium hydroxide, one of water, six of saturated mercuric chloride

solution, and once again with water. The remaining oil was dried over calcium chloride and fractionated carefully through a 23-plate column. Two clean-cut fractions resulted. The lower-boiling one (5.5 ml.) was identified by its infrared spectrum as benzene. The other was clearly decalin. No diene was obtained.

It should be pointed out here that one of the pyrolysis products of bicyclo(2,2,2)-2,5-octadiene is benzene, and benzene is also obtained as a by-product in the successful preparation of the diene, already described. The other pyrolysis product is ethylene; and no provision was made here to collect any gas that might have been evolved.

APPENDICES

APPENDIX I

PHYSICAL PROPERTIES OF COMPOUNDS[1]

COMPOUND	M. P.	B. P.[2]	REF. INDEX[3]	DENSITY[3]
Bicyclo(2,2,1)heptane	88-90	104.5	—	—
Bicyclo(2,2,1)heptene	80-85	95.5	—	—
Bicyclo(2,2,1)2,5-heptadiene	(liquid)	89.5	1.467 (26)	1.8992 (26)
2-acetoxybicyclo(2,2,1)-5-heptene	(liquid)	73-77 (14)	1.467 (30)	1.063 (32)
2-hydroxybicyclo(2,2,1)-5-heptene	108-109	—	—	—
2-chlorobicyclo(2,2,1)-5-heptene	(liquid)	46-47 (12)	1.4938 (25)*	—
2,3-dichlorobicyclo(2,2,1)-5-heptene	(liquid)	70-76 (11)	1.511 (30)	1.258 (32)

[1]The starred values are taken from the literature without confirmation; they may be found in the literature by referring to the compound in question in the body of this dissertation. All other values were determined or confirmed by the writer.

[2]Boiling points were determined at the pressures indicated (mm. of mercury). Where no pressure is given, atmospheric pressure is to be understood.

[3]Refractive indices and densities were determined at the temperatures indicated (degrees Centigrade).

PHYSICAL PROPERTIES OF COMPOUNDS (Continued)

2-chlorobicyclo(2,2,1)heptane	-5*	52 (11)*	1.480 (30)	—
2-bromobicyclo(2,2,1)heptane	—	81-83 (30)*	—	—
2-hydroxybicyclo(2,2,1)heptane	149-150	176-180	—	—
Bicyclo(2,2,2)octane	168	—	—	—
Bicyclo(2,2,2)-2-octene	99-105	132	—	—
Bicyclo(2,2,2)-2,5-octadiene	(liquid)	126	1.4912 (23)	0.9171(32)
2-acetoxybicyclo(2,2,2)-5-octene	(liquid)	138-140 (40)	1.4989 (24)	1.096 (32)
2-hydroxybicyclo(2,2,2)-5-octene	160-162	—	—	—
2-chlorobicyclo(2,2,2)octane	104-107	—	—	—
2-bromobicyclo(2,2,2)octane	64-65.6	—	—	—
2-hydroxybicyclo(2,2,2)octane	216*	—	—	—
2-chlorobicyclo(3,2,1)-3-octene[4]	(liquid)	80-90 (? mm.)	1.5160 (20)	—
2-t-butoxybicyclo(3,2,1)-3-octene[4]	(liquid)	135 (110)	1.4750 (20)	—

[4]Assumed structure, not proven as of this writing.

APPENDIX II

ULTRAVIOLET SPECTRA

The curves in this section represent the ultraviolet absorption spectra of the compounds indicated. All spectra were obtained with a Beckman model DU spectrophotometer, equipped with quartz optics and cells and a photomultiplier detector tube.

All samples were run as approximately 0.001 M. solutions in 95 per cent ethanol, with the same 95 per cent ethanol in the reference cell.

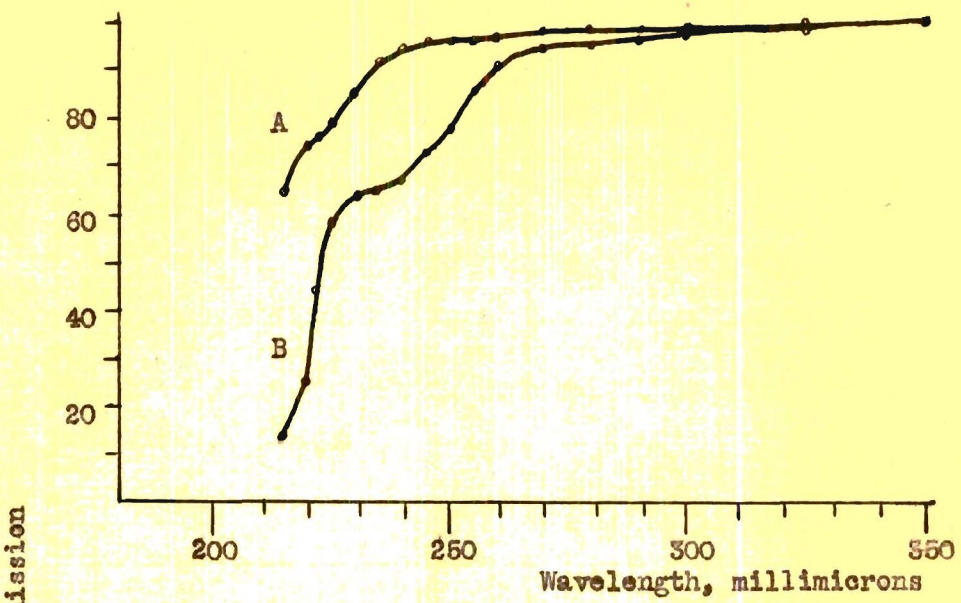

FIGURE 2. A - Bicyclo(2,2,1)-2-heptene
B - Bicyclo(2,2,1)-2,5-heptadiene

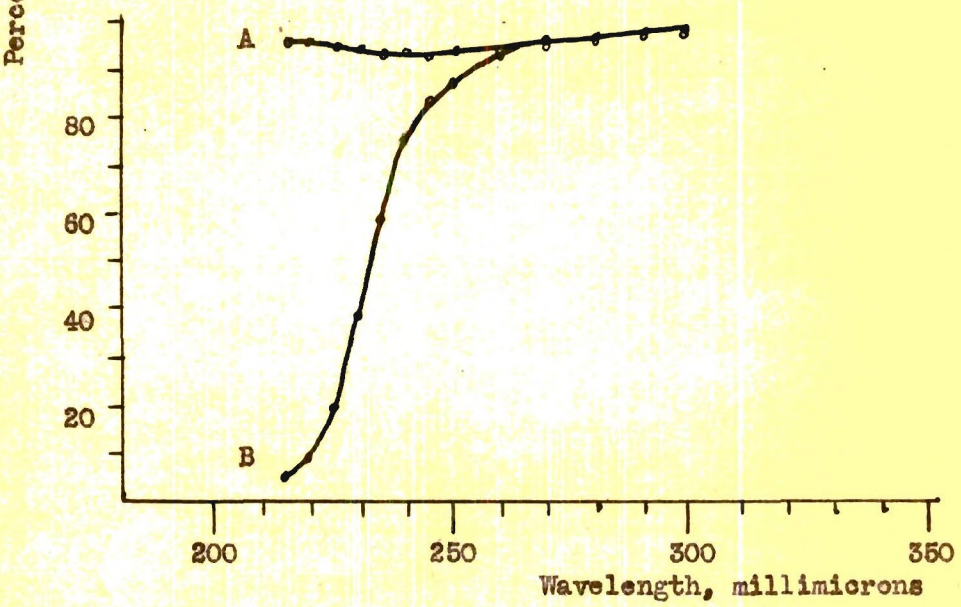

FIGURE 3. A - Bicyclo(2,2,2)-2-octene
B - Bicyclo(2,2,2)-2,5-octadiene

APPENDIX III

INFRARED SPECTRA

The curves in this section represent the infrared absorption spectra of the compounds indicated. All spectra were obtained with a Perkin-Elmer model 21 recording spectrophotometer, using sodium chloride optics and prism, a slit program of "927" which gives slit widths ranging from 12 microns at a wavelength of two microns to 280 microns at a wavelength of 14 microns, and a scanning speed of approximately one micron per minute.

These curves were prepared by transferring the original recordings to file-cards by means of hand tracing with a pantograph pen, and then tracing the reduced curves onto the final page.

Preparation of the samples depended upon their physical state. All gases were run as gases in a 10-cm. gas cell at partial pressures ranging up to one atmosphere. These partial pressures were not measured; the samples were simply diluted with air until a convenient response was obtained on the recorder. All liquids were run as pure liquids in cells of 0.1 of 0.025 cm. thickness, depending upon the strength of the absorptions. Solids were dissolved in a solvent, usually carbon disulfide, and run in cells of

thickness chosen to give a convenient response. The concentration of the solutions was not measured, but was on the order of magnitude of 25 per cent. In the case of solutions, the compensation cell of the instrument contained the pure solvent.

These curves present the spectra as per cent transmission (ordinates) plotted against the wavelength of the exciting radiation (abcissas). They are presented in alphabetical order and the legends indicate whether the sample was liquid, solution, or gas.

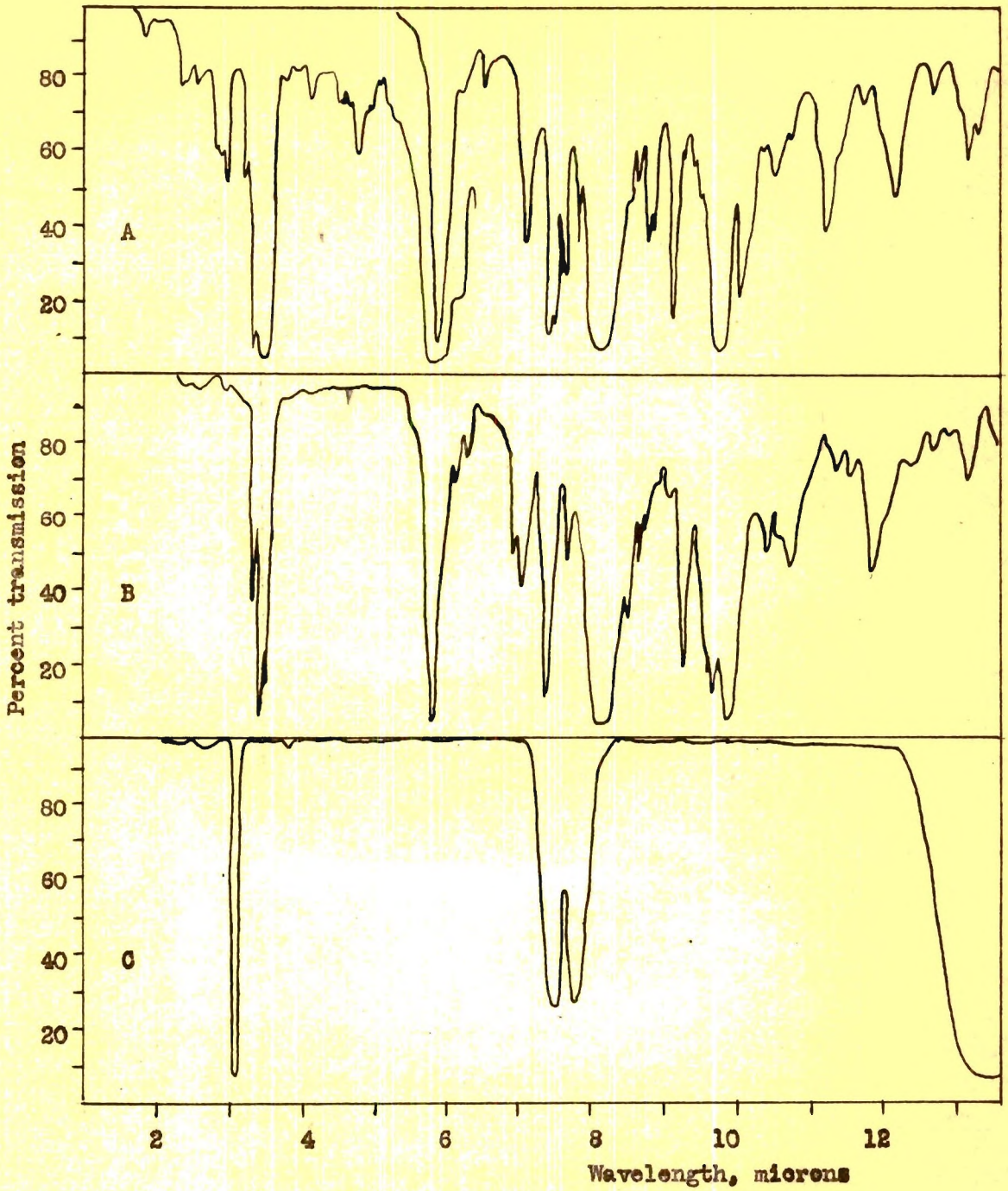

FIGURE 4. A - 2-acetoxybicyclo(2,2,1)-5-heptene (liquid)
B - 2-acetoxybicyclo(2,2,2)-5-octene (liquid)
C - Acetylene (gas)

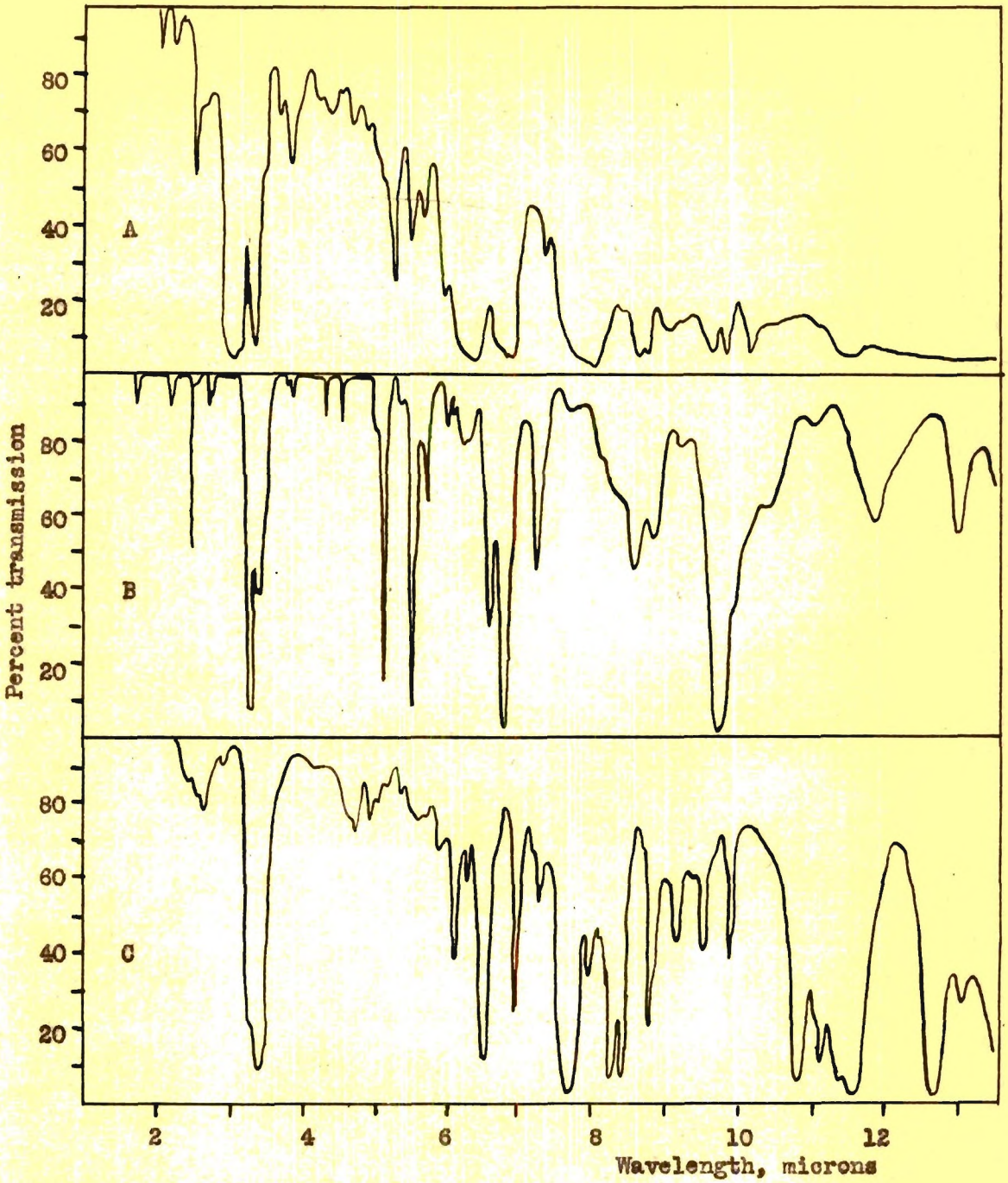

FIGURE 5. A - aniline (liquid)
B - benzene (liquid)
C - bicyclo(2,2,1)-2,5-heptadiene (liquid)

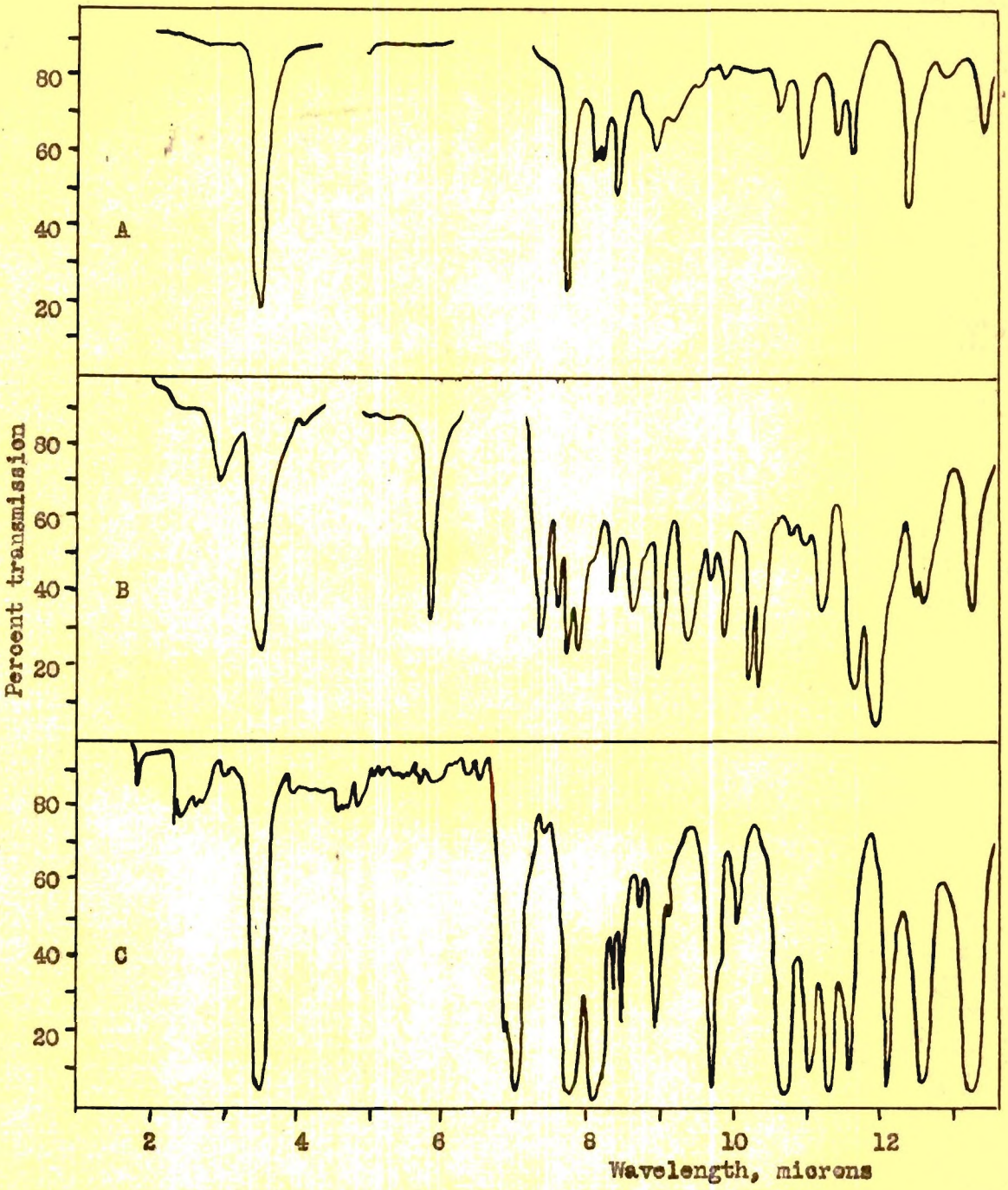

FIGURE 6. A - bicyclo(2,2,1)heptane (soln. in carbon disulfide)
B - bicyclo(2,2,1)-2-heptene (soln. in carbon disulfide)
C - 2-chlorobicyclo(2,2,1)heptane (liquid)

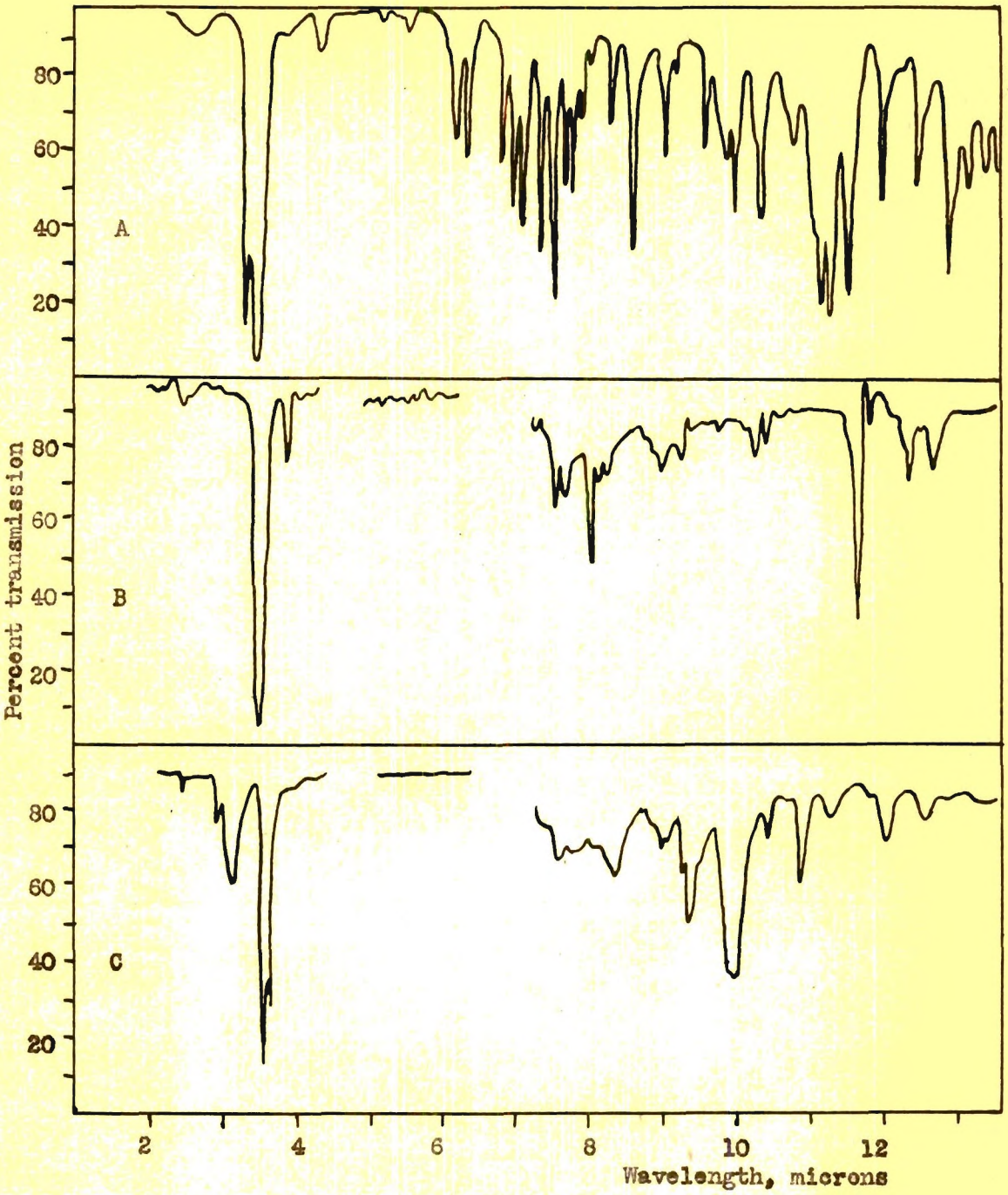

FIGURE 7. A - bicyclo(2,2,2)-2,5-octadiene (liquid)
B - bicyclo(2,2,2)octane (soln. in carbon disulfide)
C - 2-hydroxybicyclo(2,2,2)octane (soln. in carbon disulfide)

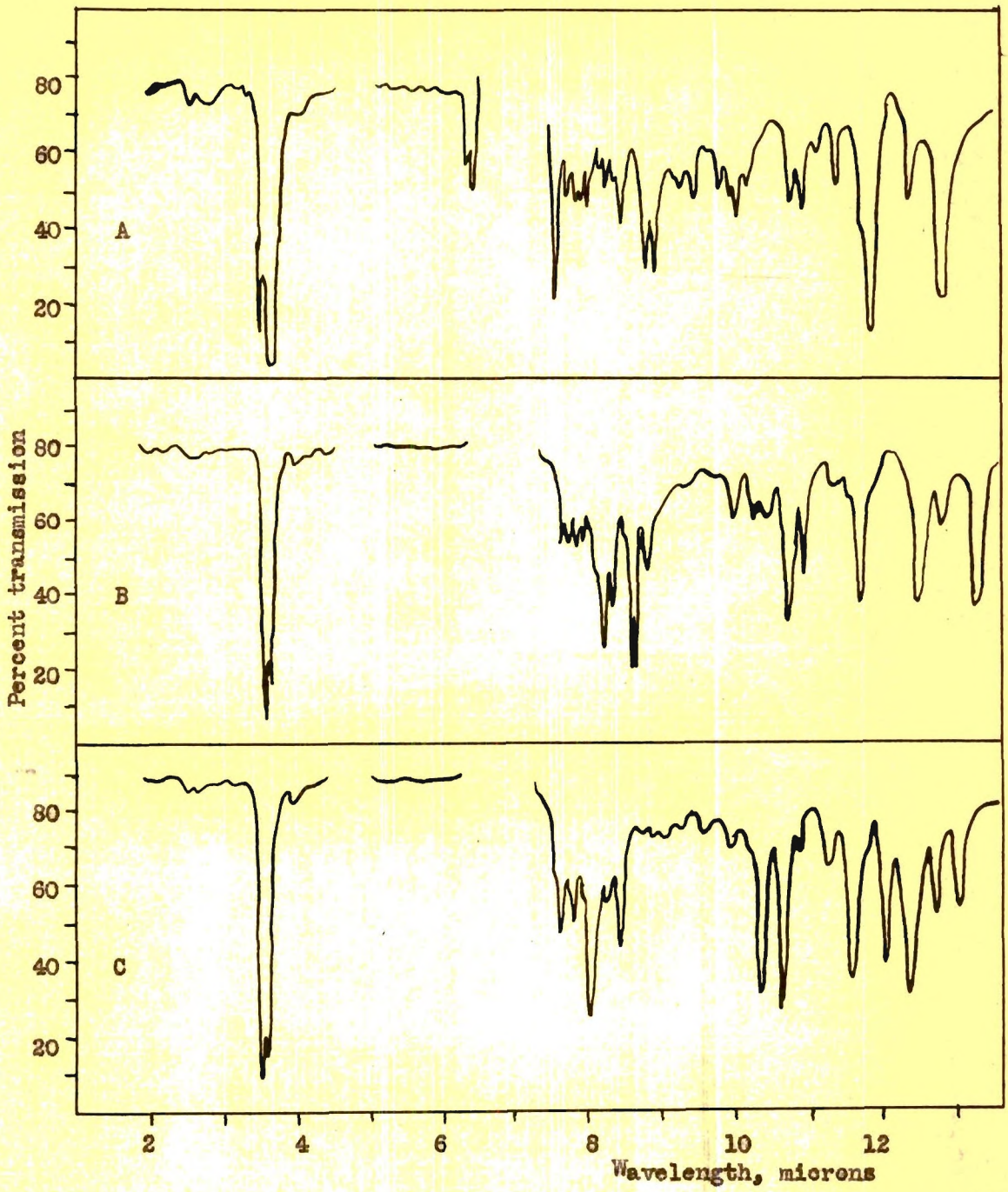

FIGURE 8. A - bicyclo(2,2,2)-2-octene (soln. in carbon disulfide)
B - 2-bromobicyclo(2,2,2)octane (soln. in carbon disulfide)
C - 2-chlorobicyclo(2,2,2)octane (soln. in carbon disulfide)

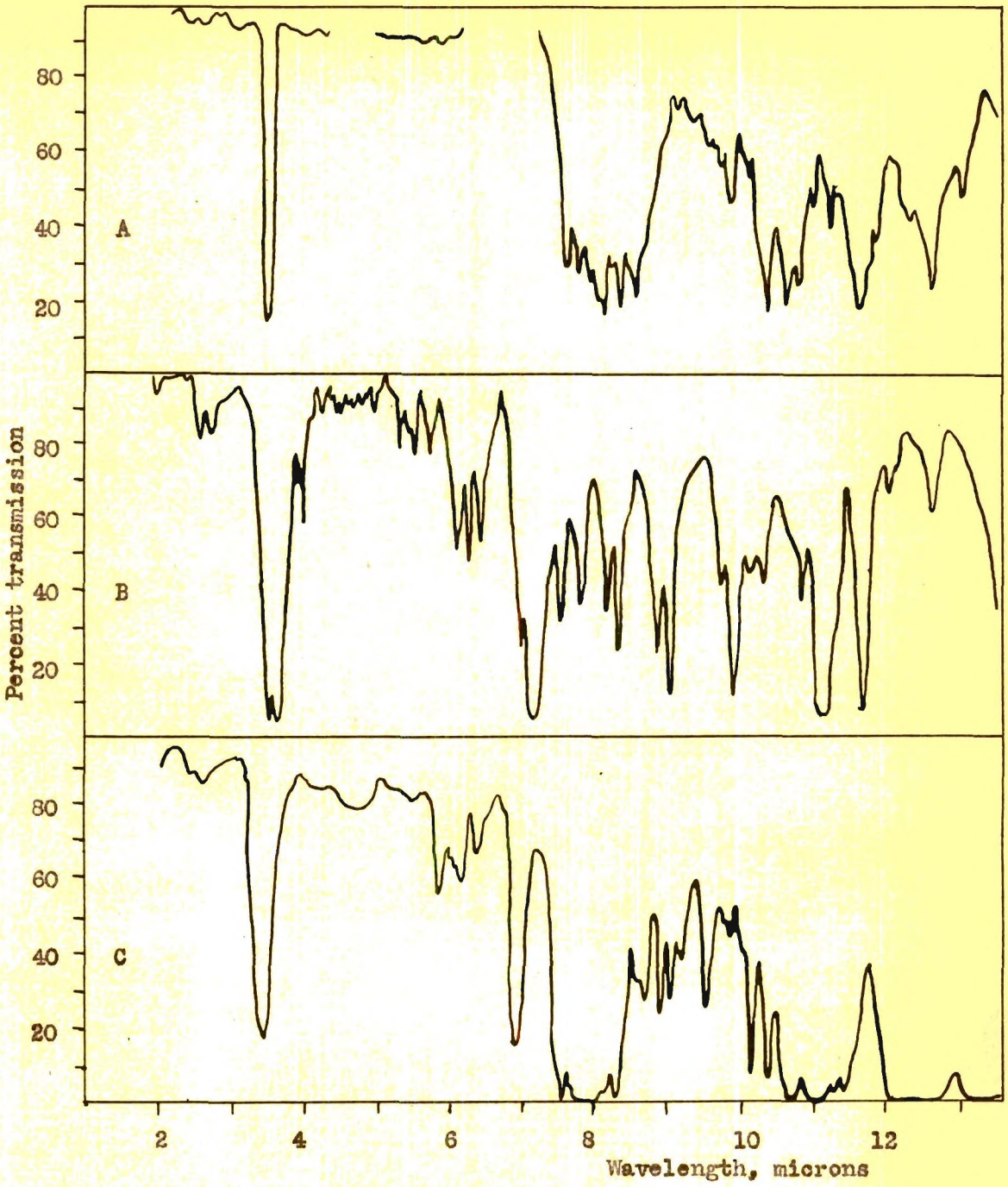

FIGURE 9. A - chloro-2-bromobicyclo(2,2,2)octane (soln, in carbon disulfide)
B - 1,3-cyclohexadiene (liquid)
C - 2,3-dichlorobicyclo(2,2,1)-5-heptene (liquid)

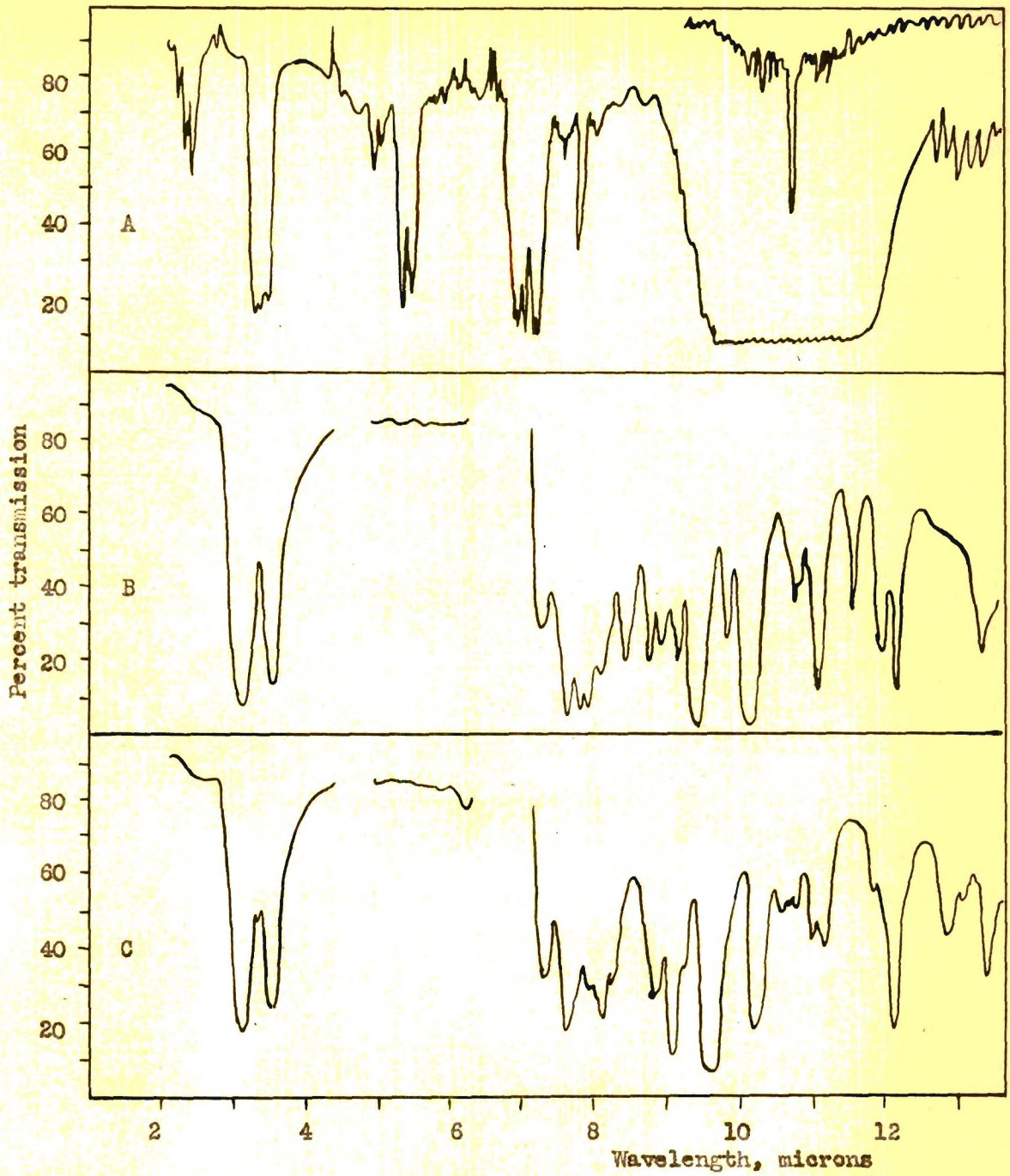

FIGURE 10. A - ethylene (gas)
B - 2-hydroxybicyclo(2,2,1)heptane (soln. in carbon disulfide)
C - 2-hydroxybicyclo(2,2,1)-5-heptene (soln. in carbon disulfide)

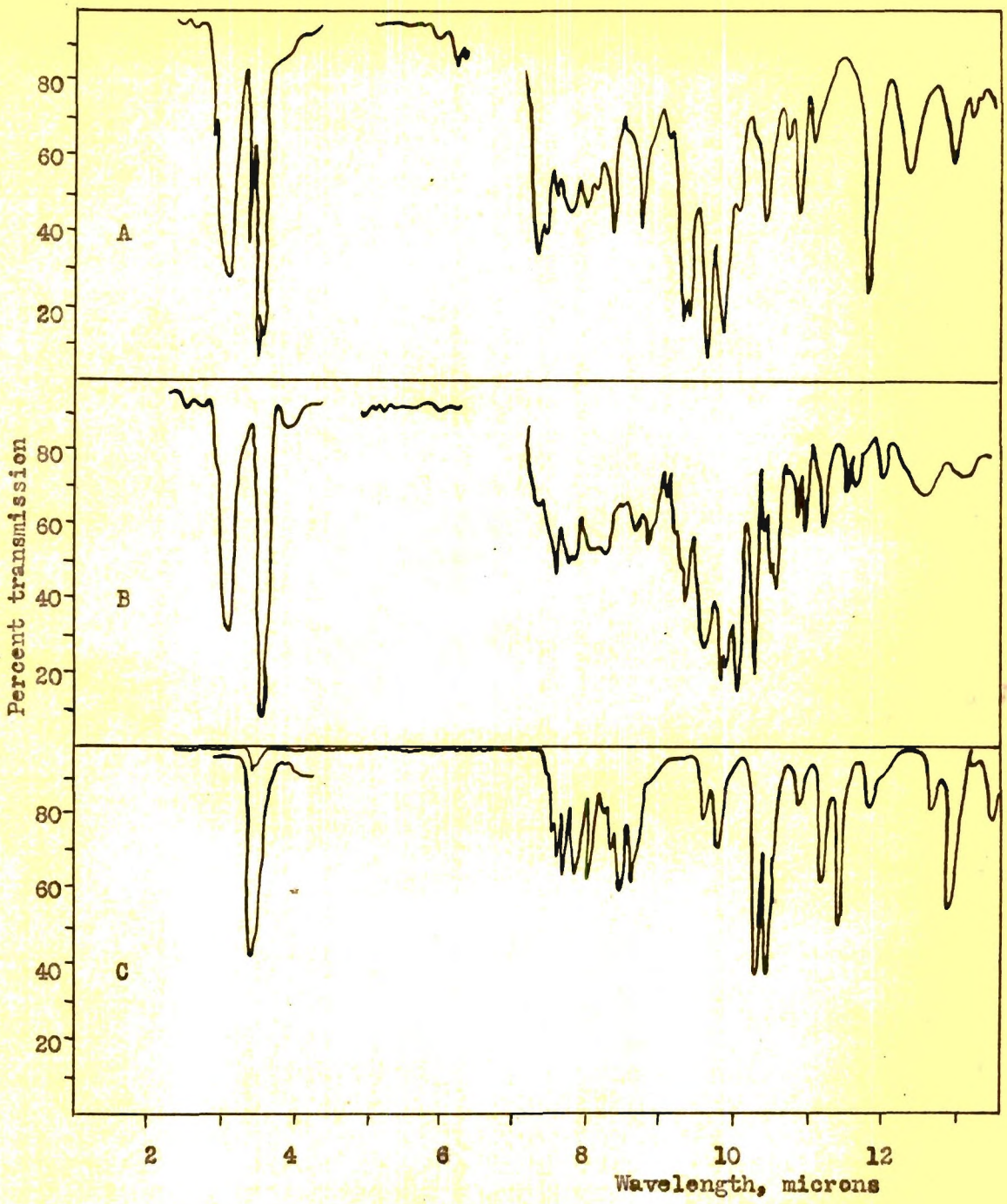

FIGURE 11. A - 2-hydroxybicyclo(2,2,2)-5-octene (soln. in carbon disulfide)
B - 2-hydroxybicyclo(3,2,1)octane (Soln. in carbon disulfide)
C - 2,3,5,6-tetrabromobicyclo(2,2,2)octane (soln in carbon disulfide)

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BIOGRAPHICAL SKETCH

John Angus Brown was born December 13, 1925, in Lake Wales, Florida, the son of Charles T. Brown and Sylva M. Brown (nee Walker). Upon graduation from high school in June of 1942, he entered Emory University, in Atlanta, Georgia, and received the A. B. degree in chemistry in June of 1945. He was employed for three years by the firm of Law and Company, Chemists, of Atlanta, Georgia, working for one year as an analytical chemist and for two years as a materials-testing engineer. In September of 1948, he entered the Graduate Division of the Georgia Institute of Technology. After receiving the degree of Master of Science in organic chemistry from the Institute in June of 1951, he remained enrolled in order to work towards the degree of Doctor of Philosophy. During his final year in graduate school, he married the former Miss Louise Rebecca Lever, of Decatur, Georgia. In August of 1954, he accepted a position as research chemist in the Research Division of the Standard Oil Development Company in Linden, New Jersey.

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